



# Sulfated titania [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>]: A very active solid acid catalyst for the esterification of free fatty acids with ethanol

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## ABSTRACT

Sulfated titanias were prepared by using ammonium sulfate and sulfuric acid as sulfate precursors. Depending on the sulfation method, important effects on the acidity, textural properties as well as on activity were found. After ammonium sulfate was used, a large amount of S=O linked to the titania surface was observed by FTIR spectroscopy. The acidity strength determined with Hammett indicators showed strong acidity in the sulfated samples. The FTIR–pyridine adsorption spectra evidenced the presence of Lewis and Brønsted acid sites in the catalysts sulfated with ammonium sulfate, while in the titania sulfated with sulfuric acid, only Lewis-type sites were observed. The sulfated titanias showed very high activity for the esterification of fatty acids with ethanol in a mixture of oleic acid (79%). Conversions up to 82.2% of the oleic acid and selectivity to ester of 100% were reached after 3 h of reaction at 80 °C. The results showed that sulfated titanias are promising solid acid catalysts to be used in the esterification of free fatty acids with ethanol.

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## 1. Introduction

The esterification of carboxylic acids with alcohols is a typical reaction in organic synthesis. Esters are obtained and used in the synthesis of drugs, food preservatives, solvents, perfumes, cosmetics and as biofuels. The latter are typically produced by either the esterification of fatty acids or the transesterification of vegetable oil. The esterification of free carboxylic acids is carried out by using proton-donor mineral acids such as sulfuric acid, p-toluene, sulphonic acid and hydrochloric acid, among others, as catalysts. However, these acid catalysts promote corrosion in the reaction units and are very difficult to be removed from the reaction medium [1]. Nowadays, the replacement of mineral acids by solid acid catalysts in order to avoid important corrosion effects, catalyst separation and pollution problems has been an important subject for many laboratories worldwide. Solid acids offer the advantages of easy catalyst separation and low pollution effects. In this way, solid acids like zeolites, resins of the type Naftion-M, zirconium sulfate on silica and Amberlys-15 have been recently reported as very active catalysts for the esterification of oleic acid [2]. Alternatively, sulfated titania has shown to be a good acid solid catalyst for a large number of reactions: isomerization [3], acylation of aromatics [4],

alkylation [5], acylation of Friedel–Crafts [6], esterification [7], photocatalytic oxidation [8], olefin oligomerization [9], decomposition of 2-propanol [10] and transesterification of vegetable oils [11]. It seems that sulfated titania develops important acidity and because of this property, it has become a promising acid solid catalyst to carry out the esterification of fatty acids.

With this in mind, in the present study, the synthesis of sulfated titanias by the sol–gel method and their evaluation in the esterification of oleic acid is reported. The sulfated titanias [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>] were synthesized by using titanium alkoxide and two different sulfate sources (sol–gel method). The characterization of the sulfated solids was performed by means of various techniques such as infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The acidic properties of the synthesized catalysts were evaluated by titration of the solids with n-butylamine, using bromothymol blue and methyl red as indicators [12]. The assessment of the catalysts was carried out in the esterification of a mixture of fatty acid with ethanol.

## 2. Experimental

### 2.1. Synthesis of catalysts

In order to study the variation of acid strength regarding the amount and method used for adding sulfate ions to the system, sulfuric acid [H<sub>2</sub>SO<sub>4</sub>] and ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] were used as precursors of sulfate ions. Ammonium sulfate was added by two

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different methods: “in situ” and impregnation. In this work, four titanias were synthesized by the sol–gel method: reference titania [TiO<sub>2</sub>–HNO<sub>3</sub>], sulfated titania by incipient impregnation with ammonium sulfate [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>–(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>], “in situ” sulfated titania with sulfuric acid [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>–H<sub>2</sub>SO<sub>4</sub>] and “in situ” sulfated titania with ammonium sulfate [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>–(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>–IS].

#### 2.1.1. Reference titania [TiO<sub>2</sub>–HNO<sub>3</sub>]

In a round-bottom flask, 13.6 mL of a mixture of distilled water (4.1 mL) and tert-butanol (9.5 mL) were added. Afterwards, the pH of the solution was adjusted with nitric acid at a value of 3. After vigorous stirring for 60 min, 16.5 mL of a solution of titanium(IV) butoxide in tert-butanol were added dropwise to the solution with constant stirring; then, the gelling solution was set under reflux at 90 °C with constant stirring for 48 h. Afterwards, the sample was dried for 24 h. The obtained solid was then separated into two portions; one portion was calcined at 400 °C for 4 h and the other one was separated to be impregnated with ammonium sulfate.

#### 2.1.2. Sulfated titania by impregnation

##### [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>–(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>–I]

The impregnation was made by adding 1 g of the reference titania to 10 mL of an aqueous solution of ammonium sulfate (1N); then the mixture was vigorously stirred at 500 rpm for 4 h at 25 °C. Afterwards, the sample was dried for 24 h and then the solid was calcined at 400 °C for 4 h.

#### 2.1.3. “In situ” sulfated titania with sulfuric acid

##### [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>–H<sub>2</sub>SO<sub>4</sub>–IS]

The same procedure performed for the reference titania was followed, but the nitric acid was replaced by concentrated sulfuric acid to adjust the pH at 3. Sulfate ions were introduced in this way into the reactant system.

#### 2.1.4. “In situ” sulfated titania with ammonium sulfate

##### [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>–(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>–IS]

In a round-bottom flask, 13.6 mL of a mixture of distilled water (4.1 mL) and tert-butanol (9.5 mL) were placed; then the solution pH was adjusted at a value of 3 by adding 0.1 mL of concentrated nitric acid. After, sulfate ions were introduced to the system by adding 10 mL of an aqueous solution containing ammonium sulfate (1N). Then the system was vigorously stirred for 60 min at 25 °C. Afterwards, 16.5 mL of a solution of titanium(IV) butoxide in tert-butanol were added dropwise to this solution under constant stirring; then, the reactant system was set under reflux at 90 °C with constant stirring for 48 h. Finally, the solid was dried for 24 h. The obtained solid was then calcined at 400 °C in air flow for 4 h.

### 2.2. Characterization of the sulfated titanias

#### 2.2.1. X-ray diffraction

The fresh and annealed sulfated titanias were characterized by powder X-ray diffraction with a RIGAKU, model D/MAX IIIIB diffractometer. A Cu target was used as X-ray source at 40 kV and 20 mA. The samples were recorded in the  $2 < 2\theta < 70$  range with a step time of 1 s and a step size of 0.02° ( $2\theta$ ).

#### 2.2.2. FTIR spectroscopy

The IR absorption spectra were obtained with a Bruker model Tensor 27 equipment in the range of 4000–400 cm<sup>-1</sup>, using KBr powders.

#### 2.2.3. BET specific surface area

Nitrogen adsorption isotherms were obtained on the sulfated titanias calcined at 400 °C, using an equipment Nova 1200 mark

Quantachrome. The surface area was calculated with the BET equation and the mean pore size diameter was calculated by using the BJH method.

#### 2.2.4. Titration method with n-butylamine using Hammett indicators

The surface acidity and acid strength of the catalysts were determined by titration with n-butylamine using the Hammett indicators. The titration was carried out by dispersing 0.05 g of catalyst in 5 mL of dry benzene; two indicator drops in benzene solution were then added to the resulting dispersed solution and the titration was done with a solution of n-butylamine (0.01N). The acidity was calculated in mole of acid sites per gram of catalyst and the acidity strength was expressed in terms of the Hammett acidity ( $H_0$ ) [13].

#### 2.2.5. Decomposition of 2-propanol

The 2-propanol reaction was carried out in a tubular glass flow reactor (3 mL) under atmospheric pressure. Prior to the reaction test, the catalyst (0.1 g) was pretreated at 120 °C for 1 h with N<sub>2</sub> flow (20 mL/min). To carry out the decomposition, 2-propanol vapor was supplied into the reactor by bubbling nitrogen gas through the alcohol container at 25 °C. The reaction temperature was 120 °C. The products were analyzed with an on-line Agilent 6890 gas chromatograph equipped with an HP-InnoWax Polyethyleneglycol column.

#### 2.2.6. FTIR-pyridine adsorption

The type and quantity of acid sites (Brönsted and/or Lewis) were determined with a Fourier transform infrared (FTIR) Nicolet Nexus 479 FT-IR spectrometer by means of pyridine adsorption. The annealed material was pressed into thin self-supported wafers. Then, they were placed in a glass Pyrex cell with CaF<sub>2</sub> windows coupled to a vacuum line in order to be evacuated ( $1 \times 10^{-6}$  Torr) in situ at 400 °C for 30 min. The adsorption was carried out on the cell at 25 °C by breaking a capillary tube, which contained pyridine. The excess pyridine was desorbed with vacuum from room temperature to 400 °C with 100 °C steps [10].

#### 2.2.7. Thermogravimetric analysis

A Seiko Exstar 6300 thermal analysis instrument was used to study the thermal evolution of the catalyst precursors. The samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min under static air.

### 2.3. Catalytic evaluation

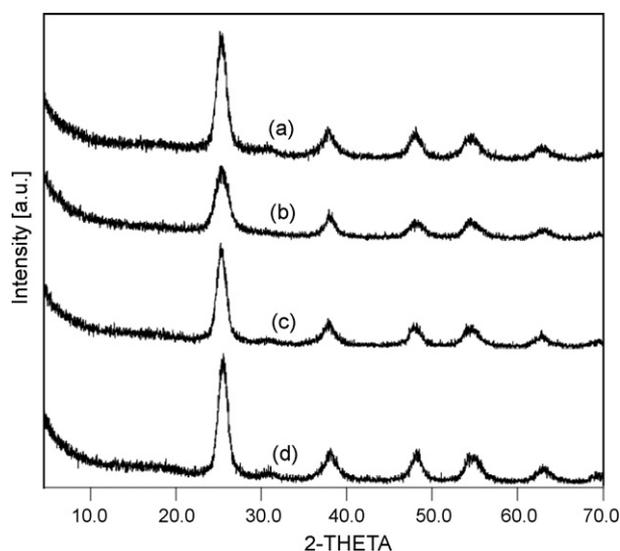
The esterification reactions were carried out under reflux at 80 °C and constant stirring (250 rpm). 2.0 g of the oleic acid mixture Carlo Erba (79%) and a fatty acids:ethanol molar ratio of 1:10 were used. The weight of the used catalyst was 2% over the initial weight of the mixture of fatty acids. The analysis of the products was made at various time intervals. The samples taken from the reactant system were analyzed by gas chromatography using an Agilent 6890 gas chromatograph equipped with an HP-InnoWax Polyethyleneglycol capillary column (30 m × 0.320 mm × 0.25 μm).

## 3. Results and discussion

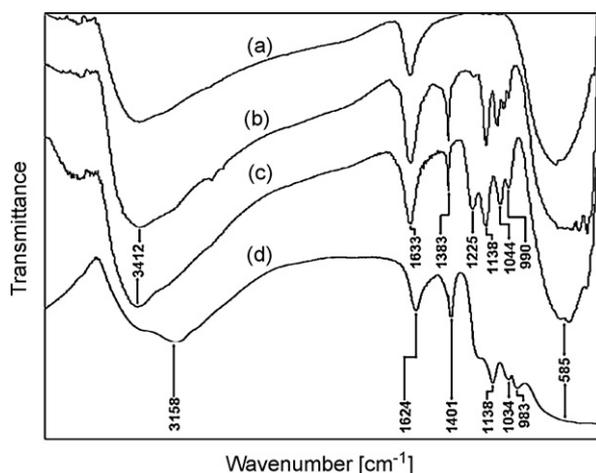
### 3.1. Characterization of catalysts

#### 3.1.1. X-ray diffraction

The XRD patterns of the reference titania and sulfated samples annealed at 400 °C are shown in Fig. 1. All the synthesized titanias showed similar diffraction patterns. The qualitative analyses



**Fig. 1.** XRD patterns for the reference titania and sulfated titania: (a)  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-I}]$ , (b)  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-IS}]$ , (c)  $[\text{TiO}_2/\text{SO}_4^{2-}-\text{H}_2\text{SO}_4\text{-IS}]$  and (d)  $[\text{TiO}_2-\text{HNO}_3]$ .

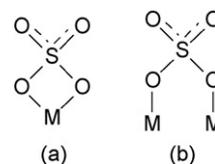


**Fig. 2.** FTIR spectra for the reference titania and sulfated titanias annealed at 400 °C: (a)  $[\text{TiO}_2-\text{HNO}_3]$ , (b)  $[\text{TiO}_2/\text{SO}_4^{2-}-\text{H}_2\text{SO}_4\text{-IS}]$ , (c)  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-I}]$  and (d)  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-IS}]$ .

of the phases present in the solids were performed by comparing the observed profile with the profiles reported in the database PDF-2 of the International Centre for Diffraction Data (ICDD). The wide peaks that appear at  $2\theta \approx 26, 38, 48, 55$  and  $66$  correspond to the anatase crystalline phase [10,14]. Ammonium sulfate cannot be observed, which suggests that the sulfate ions are highly dispersed on the surface.

### 3.1.2. FTIR spectroscopy

The infrared absorption spectra for the sulfated titanias are shown in Fig. 2. Four bands in the region between 1230 and  $980\text{ cm}^{-1}$  attributed to vibrational modes of bidentate sulfate ions



**Fig. 3.** Sulfate structures: (a) coordinated with  $C_{2v}$  chelate and (b)  $C_{2v}$  bridge.

can be seen [15,16]. In sulfated metal oxides, it has been assumed that the sulfate ion is covalently bounded to the oxide [15]. It shows  $C_{2v}$  symmetry, when it is bounded by two oxygen atoms forming chelate and bridge structures (Fig. 3).

Sohn and Kim [17] assigned the  $1225, 1138,$  and  $1044\text{ cm}^{-1}$  bands to  $\nu_3$  vibrations of bidentate  $\text{SO}_4^{2-}$  in a  $C_{2v}$  symmetry, while the band at  $990\text{ cm}^{-1}$  has been assigned to the  $\nu_1$  vibration. The bands at  $1044$  and  $990\text{ cm}^{-1}$  are assigned to asymmetric and symmetric  $\text{S}\cdots\text{O}$  stretching vibrations, respectively [15,18]. At  $1225$  and  $1138\text{ cm}^{-1}$  two bands appear due to asymmetric and symmetric stretching of  $\text{S}=\text{O}$  vibrations, respectively [15]; meanwhile, the intense band located at  $1383\text{--}1401\text{ cm}^{-1}$  has been related to the  $\text{S}=\text{O}$  stretching vibration from the sulfate ion on the surface of the solid [19,20]. The bands at  $1633$  and  $3404\text{ cm}^{-1}$  are, respectively, associated with the bending and stretching vibrations of the OH group of water molecules on the surface of the solid and with terminal OH which are characteristic of metal oxides; the band around  $585\text{ cm}^{-1}$  corresponds to  $\text{Ti}\text{--}\text{O}$  bending vibrations [15,21]. As it can be seen, the bands assigned to  $\text{S}\text{--}\text{O}$  and  $\text{S}=\text{O}$  vibrations can be observed for the sulfated titanias, while those for the reference titania are not observed. Such results confirm that in our sulfated titanias,  $\text{SO}_4^-$  appears as sulfate bonded to the titania surface.

### 3.1.3. BET specific surface area

The specific surface area, pore volume and pore diameter of the sulfated titanias are reported in Table 1. For the reference and impregnated samples, high specific surface areas of  $181$  and  $178\text{ m}^2/\text{g}$  were obtained, while for the “in situ” sulfated titania with ammonium sulfate, the specific surface area was  $48\text{ m}^2/\text{g}$ . The lowest specific surface area obtained for the “in situ” sulfated titania can be due to the modification of the hydrolysis and condensation reactions occurring during the gelling steps, since the hydrolysis rate can be modified by the presence of ammonium sulfate. As a result, different textural properties were obtained [15,22]. The sulfated titanias are almost mesoporous materials ( $>20\text{ \AA}$ ) [23,24].

### 3.1.4. Titration with *n*-butylamine using Hammett indicators

The acid strength distribution of the reference titania and sulfated titanias was determined by using the Hammett indicators shown in Table 2; the results are reported in Table 3. The positive sign (+) means that the solid presents an acid strength that is higher than that of the indicator; the negative sign (–) indicates that its acid strength is lower than that of the indicator [25].

The results show that the reference titania,  $[\text{TiO}_2-\text{HNO}_3]$ , had an acid strength of  $H_0 \leq +4.8$ , which is the  $H_0$  value for methyl red, meanwhile the  $[\text{TiO}_2/\text{SO}_4^{2-}-\text{H}_2\text{SO}_4\text{-IS}]$  had an acid strength of  $H_0 \leq +1.2$ . On the other hand, the sulfated titanias

**Table 1**  
Specific surface area, pore volume and mean pore size diameter of sulfated titania annealed at 400 °C.

Titania	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore diameter ( $\text{\AA}$ )	$\text{mmol SO}_4^-/\text{g [TGA]}$
$[\text{TiO}_2-\text{HNO}_3]$	181	0.237	52	–
$[\text{TiO}_2/\text{SO}_4^{2-}-\text{H}_2\text{SO}_4\text{-IS}]$	196	0.278	57	0.1
$[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-I}]$	48	0.0446	18	1.3
$[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-IS}]$	178	0.188	42	1.1

**Table 2**  
Hammett indicators used in titrations.

Indicator	$H_0$	Acid color	Basic color
Bromothymol blue	$\leq +7.2$	Yellow	Blue
Methyl red	$\leq +4.8$	Red	Yellow
Cresol bromine green	$\leq +3.8$	Yellow	Blue
Thymol blue	$\leq +1.2$	Red	Yellow
Crystal violet	$\leq +0.8$	Yellow	Blue

**Table 3**  
Distribution of acid strength of sulfated titanias using Hammett indicators.

Titania	$H_0$ value				
	$\leq +7.2$	$\leq +4.8$	$\leq +3.8$	$\leq +1.2$	$\leq +0.8$
[TiO <sub>2</sub> -HNO <sub>3</sub> ]	+	+	–	–	–
[TiO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup> -H <sub>2</sub> SO <sub>4</sub> -IS]	+	+	+	+	–
[TiO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup> -(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> -IS]	+	+	+	+	+
[TiO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup> -(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> -I]	+	+	+	+	+

[TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-IS] and [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-I] show a large distribution of acid strength ( $H_0 \leq +0.8$ ).

The increased acidity obtained on sulfated titanias was also reported by several authors who proposed that the formation of the acid sites in these solids is favored by the presence of S=O linked to the titania surface [26–29]. The identification and characterization of the acid sites (Lewis and/or Brönsted) has been made by different techniques such as pyridine adsorption [8–10] and thermal programmed desorption of basic molecules [30].

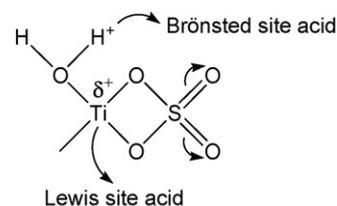
### 3.1.5. Decomposition of 2-propanol

The dehydration of 2-propanol was carried out for the reference titania and sulfated titanias as an indirect test to determine their acidity, and the results are reported in Table 4.

It can be seen that the total conversion rate follows the sequence: [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-I] > [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-IS] > [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>SO<sub>4</sub>-IS] > [TiO<sub>2</sub>/HNO<sub>3</sub>]. The isopropanol decomposition has been extensively reported as a valuable catalytic test to analyze the acid–basic properties of heterogeneous catalysts. In general, it is conventionally accepted that the acid sites are the responsible for the dehydration activity giving propene and isopropyl ether as products. Similarly, for the formation of the dehydrogenated product (acetone), acid and basic sites are required. The sulfated catalysts did not show basic sites, since acetone was not obtained as product. The [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-I], [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-IS] and [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>SO<sub>4</sub>-IS] catalysts showed acid properties since propene and DIPE were formed. The results of the [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-I] and [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-IS] catalysts show that the strength of the acid sites depends on the sulfating method. The amount of added sulfate ions is also an important acidity factor as it is demonstrated by the low catalytic activity of the [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>SO<sub>4</sub>-IS] sample. Even when the exact nature of the acid sites on the sulfated titania is not known, we can expect that both Lewis and Brönsted acid sites can be developed on sulfated titania according to the model presented in Fig. 4. The acid strength is remarkably increased because of the inductive effect on the S=O bonds.

**Table 4**  
2-Propanol dehydration at 120 °C on the sulfated titanias annealed at 400 °C.

Catalyst	Rate [mol/mg s]	% Se	
		Propene	DIPE
[TiO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup> -(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> -I]	$4.91 \times 10^{-4}$	87.18	12.82
[TiO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup> -(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> -IS]	$1.13 \times 10^{-4}$	86.41	13.59
[TiO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup> -H <sub>2</sub> SO <sub>4</sub> -IS]	$5.33 \times 10^{-6}$	100	0
[TiO <sub>2</sub> /HNO <sub>3</sub> ]	0	0	0

**Fig. 4.** Schematic representation of the Brönsted and Lewis acid sites present in the sulfated titania.

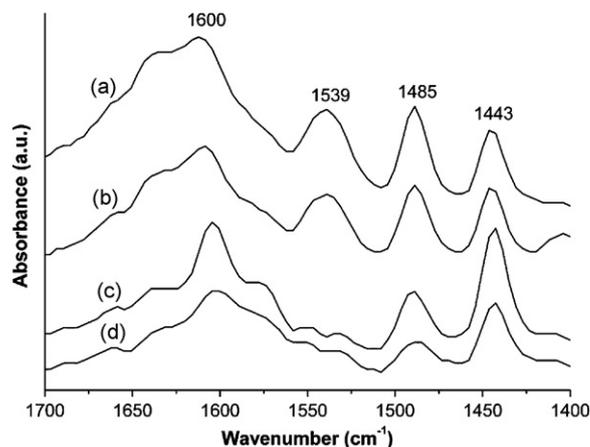
### 3.1.6. FTIR-pyridine adsorption

The FTIR-pyridine thermodesorption spectra of the sulfated titanias are presented in Fig. 5. The reference titania [TiO<sub>2</sub>-HNO<sub>3</sub>] and “in situ” sulfated titania with sulfuric acid [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>SO<sub>4</sub>-IS] show a band around 1443 cm<sup>-1</sup>, which is assigned to the adsorption of coordinated pyridine in Lewis sites. The sulfated titania prepared by impregnation [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-I] and “in situ” sulfated titania [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-IS] show in addition to Lewis acid site absorption bands, the band around 1539 cm<sup>-1</sup> assigned to the presence of Brönsted acid sites in the solids. The pyridinium ions are formed by the transfer of protons from the acidic hydroxyl groups in the material to the organic base. All the catalysts show a band around 1600 cm<sup>-1</sup>. This band indicates the formation of strong Lewis acid sites. In Fig. 6, the semi-quantitative evaluation of the acid site concentration calculated from the integrated bands is reported. In Fig. 6, it can be seen that the [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-I] catalyst developed the highest quantity of acid sites. Meanwhile the [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>SO<sub>4</sub>-IS] and [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-IS] catalysts show a similar concentration of acid sites.

## 3.2. Catalytic evaluation

The catalytic evaluation was carried out and the evolution of the conversion of oleic acid as a function of time is reported in Fig. 7. All the catalysts showed 100% selectivity in the esterification reaction of fatty acids, as it can be evidenced by the gas chromatography analysis of the products as shown in Fig. 8, where only the unreacted acids and the corresponding esters can be identified. The activity for the various catalysts after 3 h in stream is reported in Table 5, where it can be seen that good correlations concerning the activity for oleic acid esterification and 2-propanol dehydration were obtained.

In the analysis of the acidic properties, we found that the amount of sulfate ions added to the system is the fundamental factor for

**Fig. 5.** FTIR-pyridine adsorption for the reference titania and sulfated titanias annealed at 400 °C: (a) [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-I], (b) [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-IS], (c) [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>SO<sub>4</sub>-IS] and (d) [TiO<sub>2</sub>-HNO<sub>3</sub>].

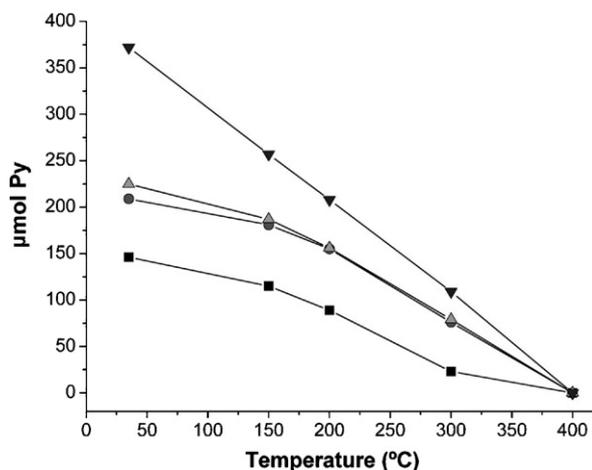


Fig. 6. Adsorbed pyridine ( $\mu\text{mol/g}$ ) in all synthesized titanias annealed at  $400\text{ }^\circ\text{C}$ : ( $\nabla$ )  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-I}]$ , ( $\Delta$ )  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-IS}]$ , ( $\bullet$ )  $[\text{TiO}_2/\text{SO}_4^{2-}-\text{H}_2\text{SO}_4\text{-IS}]$ , and ( $\blacksquare$ )  $[\text{TiO}_2-\text{HNO}_3]$ .

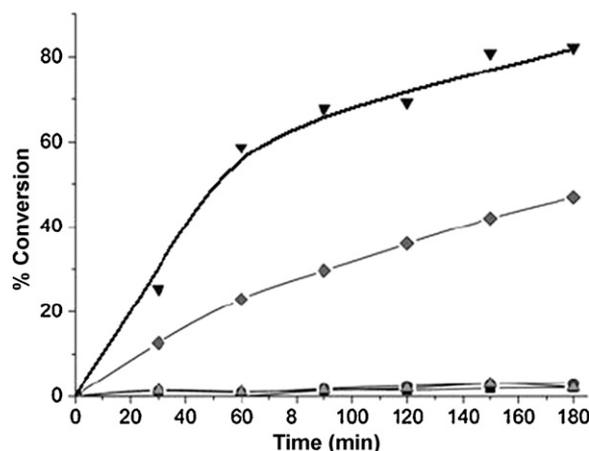


Fig. 7. Activity of sulfated titanias: ( $\nabla$ )  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-I}]$ , ( $\blacklozenge$ )  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-IS}]$ , ( $\blacktriangle$ )  $[\text{TiO}_2/\text{SO}_4^{2-}-\text{H}_2\text{SO}_4\text{-IS}]$ , ( $\bullet$ )  $[\text{TiO}_2-\text{HNO}_3]$ , and ( $\blacksquare$ ) without catalyst.

increasing the acid strength of sulfated titania. This is reflected in the sulfated titania catalytic activity in the esterification reaction of free fatty acids and the decomposition of 2-propanol. The lowest activity corresponds to the catalyst with the lowest sulfate concentration (Table 1).

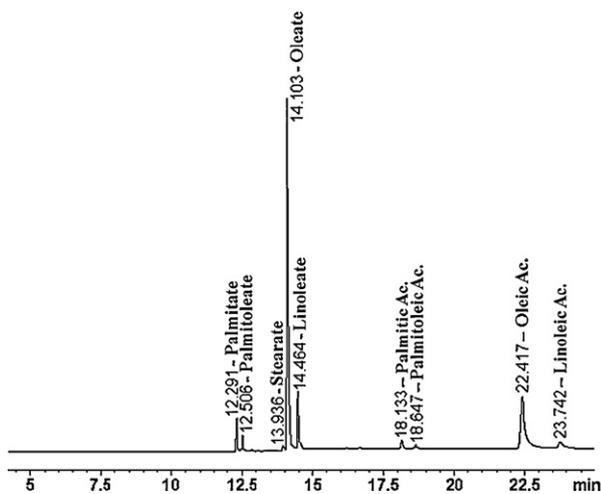


Fig. 8. Gas chromatography analysis for the esterification of fatty acids.

Table 5

Relationship between the conversion of 2-propanol and oleic acid esterification on sulfated titania.

Titania	% Conversion	
	2-Propanol	Oleic acid
$[\text{TiO}_2-\text{HNO}_3]$	0	3.1
$[\text{TiO}_2/\text{SO}_4^{2-}-\text{H}_2\text{SO}_4]$	0.5	2.1
$[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-IS}]$	10.54	47.0
$[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-I}]$	46.06	82.2

The “in situ”  $[\text{TiO}_2/\text{SO}_4^{2-}-\text{H}_2\text{SO}_4\text{-IS}]$  sulfated sample, in spite of possessing the highest specific surface area, presents an acid strength between +1.2 and +0.8 (Table 3). This acid strength is not enough to carry out the esterification reaction of fatty acids. The low acid strength of this solid can be attributed to the low amount of sulfate ions.

The impregnated titania  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-I}]$  presents the highest activity with a conversion of oleic acid of 82.2% after 3 h of reaction. On the other hand, the “in situ” prepared sample  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-IS}]$  presents a lower activity, 47% of conversion after 3 h of reaction. This can be attributed to two factors: the amount of sulfate ions on the catalysts (Table 1) and the decisive factor in the esterification reaction that is the acidity strength of the catalyst (Table 3).

Oleic and linoleic acids are converted at different initial rates; however, after 6 h of reaction, 86% of both acids are converted. Fig. 9 shows the comparison of activity for both acids, using the catalyst impregnated with ammonium sulfate  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-I}]$ .

In Table 6, a comparison of the results obtained in the esterification of oleic acid with other catalysts reported by several authors is reported. Díaz et al. [31] used mesoporous silica functionalized with sulphonic acid as catalyst and obtained a conversion of approximately 80% after 8 h of reaction; and the maximum rate, close to 100%, was reached after 24 h of reaction. The authors worked with a reaction temperature of  $120\text{ }^\circ\text{C}$  and 5 wt% of catalyst; conditions that are higher than those used in the present work. In a second study, Díaz et al. [32] used silica mesoporous materials functionalized with dialkyl silane groups as catalysts for the oleic acid esterification with glycerol; they reported 89% of conversion after 8 h of reaction.

Takagaki et al. [1] developed a solid acid from charred D-glucose obtaining a conversion of 26.4% after 1 h of reaction. In comparison with the results of the present work, the esterification carried out with the impregnated catalyst  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-I}]$  and under similar experimental conditions (molar ratio and temper-

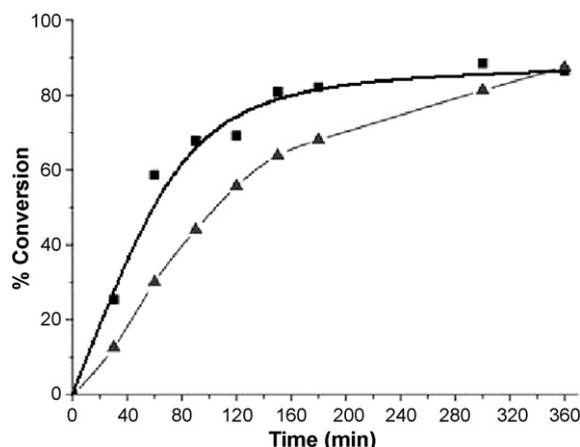


Fig. 9. Activity of impregnated titania  $[\text{TiO}_2/\text{SO}_4^{2-}-(\text{NH}_4)_2\text{SO}_4\text{-I}]$  in the conversion of oleic ( $\blacksquare$ ) and linoleic ( $\blacktriangle$ ) acids.

**Table 6**

Comparison of results obtained in the esterification of oleic acid.

Author	Catalyst	T [°C]	Molar ratio acids:alcohol	% Catalyst <sup>a</sup>	% Conversion
This work	TiO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup> -(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	80	1:10 (ethanol)	2	58.7–1 h
This work	TiO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup> -(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> -IS	80	1:10 (ethanol)	2	29.7–1.5 h
Díaz et al. [31]	SO <sub>3</sub> H-MCM-41	120	1:1 (glycerol)	5	~80–8 h
Díaz et al. [32]	[CH <sub>3</sub> ,SO <sub>3</sub> H]-MCM-41	120	1:1 (glycerol)	5	89–8 h
Takagaki et al. [1]	D-Glucose-SO <sub>3</sub> H	80	1:10 (ethanol)	7.1	26.4–1 h
Juan et al. [2]	ZrSO <sub>4</sub> -SiO <sub>2</sub>	110–120	1:1.2 (n-butanol)	5	~80–1 h
Takagaki et al. [1]	H <sub>2</sub> SO <sub>4</sub>	80	1:10 (ethanol)	7.1	93.6–1 h

<sup>a</sup> Weight percent measured with respect to the weight of the initial mixture of fatty acids.

ature) employed by Takagaki, we obtained a conversion of 58.7% after 1 h of reaction, which is higher than that obtained by this author.

In the esterification of oleic acid, using silica-supported zirconium sulfate (ZrSO<sub>4</sub>-SiO<sub>2</sub>) [2], a maximum conversion of 94% was reached after 4 h of reaction at a reaction temperature of 110–120 °C, and a catalyst amount of 5%, which exceeds the conditions employed for the sulfated titania used in the present work.

#### 4. Conclusions

The sulfated titanias calcined at 400 °C showed low crystallinity and presented only the anatase phase. It was shown that the addition of sulfate ions to titania produced solids with important acidic properties. The amount and method used for adding the sulfate ions determines the strength of the acidic properties. It is shown that ammonium sulfate is a suitable precursor for the sulfation of titania. The sulfated titania catalysts showed a high selectivity (100%) to the esterification of fatty acids. It was evidenced that the sulfated titania prepared by incipient impregnation with ammonium sulfate was the catalyst with the highest esterification activity in comparison with different acid catalysts reported in the literature.

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