

# Synthesis and characterization of trifluoromethanesulfonic acid supported on mesoporous titania

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## Abstract

Mesoporous titania materials have been synthesized by using urea as a template via sol–gel reactions of titaniumisopropoxide, followed by the removal of urea by extraction with water. The solid was dried, calcined at different temperatures and impregnated with trifluoromethanesulfonic acid. They were extracted by a mixture of dichloromethane and diethyl ether using a Soxhlet apparatus in order to remove the loosely adsorbed acid. The solids were characterized by FT-IR, XRD, DTA–TGA, and BET. The acidic characteristics of the catalysts were determined by potentiometric titration with *n*-butylamine and the test reaction of isopropanol dehydration.

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## 1. Introduction

Homogeneous acidic catalysts such as H<sub>2</sub>SO<sub>4</sub>, HCl, HF, CH<sub>3</sub>SO<sub>3</sub>H, AlCl<sub>3</sub>, and BF<sub>3</sub>, among others, are commonly used for organic synthesis carried out in laboratories and industries. However, the above-mentioned catalysts have several disadvantages because they are corrosive, toxic or volatile, and generate large amounts of waste.

In order to overcome all the drawbacks in the use of environmentally hazardous homogeneous catalysts, new solid acids such as: zeolites [1,2], clays [3], metal oxides (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, SnO<sub>2</sub>) promoted by sulfate ions [4–6], heteropolyacids and their salts [7,8] have been tested.

The use of organically functionalized mesoporous silica as a catalyst for organic synthesis has received considerable attention [9–15]. Among these materials, sulfonic acid functionalized mesoporous silicas seem to be alternatives to commercially available sulfonic resins, which suffer from low surface area and thermal stability.

Recently, mesoporous zirconium oxide was used for the heterogenization of trifluoromethanesulfonic acid [16,17], which

is a strong acid used as homogeneous catalyst in many organic reactions [18–20]. However, the recovery of acid from the reaction mixture results in the formation of large amounts of waste, which is unacceptable from an environmental point of view.

Mesoporous titania oxide synthesized via sol–gel reactions using urea as a low-cost pore-forming agent [21] presents suitable properties to be used as a catalyst support. To the best of my knowledge, there have been no reports in the literature about the use of mesoporous titania as support of trifluoromethanesulfonic acid.

In the present work the synthesis and characterization of trifluoromethanesulfonic acid supported on mesoporous titania prepared using urea as a low-cost, pore-forming agent, via HCl catalyzed sol–gel reactions is presented. The acidic characteristics of the solids were determined by potentiometric titration with *n*-butylamine and the test reaction of isopropanol dehydration.

## 2. Experimental

### 2.1. Synthesis of catalysts

#### 2.1.1. Synthesis of mesoporous titania

Titaniumisopropoxide (Aldrich, 26.7 g) was mixed with absolute ethanol (Merck, 186.6 g) and stirred for 10 min to

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obtain a homogeneous solution under  $N_2$  at room temperature, then  $0.33 \text{ cm}^3$  of 0.28 M HCl aqueous solution was dropped slowly into the above mixture to catalyze the sol–gel reaction for 3 h. After that, an appropriate amount of urea–alcohol–water (1:5:1 weight ratio) solution was added to the hydrolyzed solution under vigorous stirring to act as template. The amount of added solution was fixed in order to obtain a template concentration of 10% by weight in the final material. The gel was kept in a beaker at room temperature till dry. The solid was ground into powder and extracted by distilled water for three periods of 24 h, in a system with continuous stirring to remove urea. Finally, it was calcined at 100, 200, 300, and 400 °C for 24 h ( $Ti_{100}$ ,  $Ti_{200}$ ,  $Ti_{300}$ , and  $Ti_{400}$ , respectively).

### 2.1.2. Synthesis of supported trifluoromethanesulfonic acid

Trifluoromethanesulfonic acid,  $CF_3SO_3H$  (0.01 mol, Alfa Aesar, 99%), was added dropwise to the mixture of mesoporous titania (2 g) and toluene ( $20 \text{ cm}^3$ , Merck) at 90 °C under nitrogen atmosphere; then it was further refluxed for 2 h. Next, the sample was cooled, filtered, washed with acetone (Mallinckrot AR) and dried at 100 °C for 24 h.

The solids were extracted by a mixture of dichloromethane and diethyl ether (100 g of mixture per gram of catalyst) for three periods of 8 h using a Soxhlet apparatus in order to remove the acid weakly attached to the support. Afterwards, they were dried again at 100 °C for 24 h. The samples were named  $TriTi_{100}$ ,  $TriTi_{200}$ ,  $TriTi_{300}$ , and  $TriTi_{400}$ . The amount of trifluoromethanesulfonic acid retained was determined by elemental analysis of C and S carried out with an EA1108 Elemental Analyzer (Carlo Erba Instruments).

## 2.2. Support and catalyst characterization

### 2.2.1. Textural properties

Specific surface area of the solids was determined from  $N_2$  adsorption–desorption isotherms at liquid-nitrogen temperature. They were obtained using Micromeritics ASAP 2020 equipment. The samples were previously degassed at 100 °C for 2 h.

### 2.2.2. Fourier transform infrared spectroscopy

FT-IR spectra of supports and catalysts were obtained in the  $400\text{--}4000 \text{ cm}^{-1}$  wavenumber range using a Bruker IFS 66 FT-IR spectrometer.

### 2.2.3. X-ray diffraction

Powder XRD patterns were recorded on the same samples that had been analyzed by FT-IR. The equipment used to this end was a Philips PW-1732 with a built-in recorder, using  $Cu K\alpha$  radiation, nickel filter, 20 mA and 40 kV in the high voltage source, and scanning angle between 5 and 60° of  $2\theta$  at a scanning rate of 1° per minute.

### 2.2.4. Thermogravimetric and differential thermal analysis

The TGA–DTA measurements of the solids were carried out using a Shimadzu DT 50 thermal analyzer. The thermogravimetric and differential thermal analyses were performed under

argon or nitrogen respectively, using 25–50 mg samples and a heating rate of 10 °C/min. The studied temperature range was 20–700 °C.

## 2.3. Acidity measurements

### 2.3.1. Potentiometric titration

The acidity of the solid samples was measured by means of potentiometric titration. The solid (0.05 g) was suspended in acetonitrile (Merck), and agitated for 3 h. Then, the suspension was titrated with 0.05 N *n*-butylamine (Carlo Erba) in acetonitrile at 0.05 ml/min. The electrode potential variation was measured with a Hanna 211 digital pHmeter using a double junction electrode.

### 2.3.2. Isopropanol dehydration

The dehydration of isopropanol (Mallinckrot AR) was carried out in a conventional flow fixed bed reactor at atmospheric pressure and 100 °C. The gas carrier was helium and the isopropanol volumetric flow was  $2.1 \cdot 10^{-3} \text{ cm}^3/\text{s}$  in a total flow of  $50 \text{ cm}^3/\text{min}$ . The reaction products were quantified by gas chromatography, using a thermal conductivity detector. The specific isopropanol conversion (as turnover frequency) was calculated under differential conversion conditions. It was expressed as moles of transformed isopropyl alcohol/moles of  $CF_3SO_3H$  in the solid per second ( $SCV_{IPA}$ ).

## 3. Results and discussion

### 3.1. Support and catalyst characterization

The specific surface area ( $S_{BET}$ ) of the titania support determined from  $N_2$  adsorption–desorption isotherms together with the average pore diameter ( $D_p$ ) obtained from the BJH pore size distribution is shown in Table 1. As can be seen, all the samples are mesoporous with a  $D_p$  higher than 3.2 nm. The  $S_{BET}$  decreases when increasing the calcination temperature (Table 1). Calcination at 300 and 400 °C produces little pore narrowing. Some of the narrowest pores seem to collapse upon evolution of water forming two groups of pore size in the mesopore range.

TGA patterns of the supports show that dehydration takes place in two main steps. The first step is due to the loss of physically adsorbed water (below 160 °C) and the second to the loss of structural water in the temperature range 160 to 400 °C. For the  $Ti_{100}$  sample, the number of water molecules released per gram ( $N_w$ ) estimated from the weight loss

Table 1  
Physico-chemical properties of titania supports and trifluoromethanesulfonic acid supported catalysts

Sample	$S_{BET}$ ( $\text{m}^2/\text{g}$ )	$D_p$ (nm)	$N_w$ (molecules/g)	$N_{Tri}$ (mmol $CF_3SO_3H/\text{g}$ )	$W_{Tri}$ (mmol $CF_3SO_3H/\text{g}$ )
$Ti_{100}$	287	3.9	$1.52 \cdot 10^{21}$	–	–
$Ti_{200}$	221	4.0	$1.11 \cdot 10^{21}$	–	–
$Ti_{300}$	159	3.2–5.8	$0.51 \cdot 10^{21}$	–	–
$Ti_{400}$	124	3.9–5.9	$0.38 \cdot 10^{21}$	–	–
$TriTi_{100}$	265	3.9	–	0.84	0.86
$TriTi_{200}$	209	3.9	–	0.53	0.51
$TriTi_{300}$	151	3.2–5.7	–	0.32	0.31
$TriTi_{400}$	118	3.9–5.8	–	0.24	0.24

ascribed to the second step is  $1.52 \cdot 10^{21}$ .  $N_w$  decreases when the calcination temperature increases (Table 1), as a result of the dehydroxylation of the titania surface during the thermal treatment of the samples.

The DTA diagram of  $Ti_{100}$  showed an endothermic peak at 52 °C, associated with the loss of physically adsorbed water, and two poorly developed endothermic peaks at 310 and 370 °C attributed to the partial dehydroxylation of the titania surface. They could be considered as an indication of the presence of two types of hydroxyl groups, usually present at the titania surface [22]. DTA diagrams of  $Ti_{200}$  and  $Ti_{300}$  samples presented features similar to those of  $Ti_{100}$ . However, for the  $Ti_{400}$  sample, the endothermic peaks assigned to dehydroxylation were not detected.

The amount of acid firmly adsorbed to the support ( $N_{Tri}$ ) calculated from the elemental analysis is presented in Table 1. It is in close agreement with  $W_{Tri}$ , the amount of acid estimated from TGA diagrams (Fig. 1) and calculated using the following expression:

$$W_{Tri} = (W_{TriTi_x} - W_{Ti_x}) / FW_{Tri}$$

where:

$W_{TriTi_x}$  = weight loss of  $TriTi_x$  catalyst from 25 °C to 500 °C (mg/g)

$W_{Ti_x}$  = weight loss of  $Ti_x$  support from 25 °C to 500 °C (mg/g)

$FW_{Tri}$  =  $CF_3SO_3H$  molecular weight

$N_{Tri}$  shows a trend to decrease with the drop of  $S_{BET}$ . This can be explained if the interaction between the trifluoromethanesulfonic acid and titania is assumed to be of electrostatic type due to the transfer of protons to the –OH groups on the surface of the support. So, as result of the dehydroxylation of the support that takes place during the thermal treatment, the amount of –OH groups available to be protonated decreases, and so the amount of adsorbed acid falls.

On the other hand,  $TriTi_{100}$ ,  $TriTi_{200}$ ,  $TriTi_{300}$ , and  $TriTi_{400}$  catalysts present slightly lower  $S_{BET}$  values than those of the solids used as support. From these results, it can be seen that the decrease of  $S_{BET}$  seems to be related to the amount of trifluoromethanesulfonic acid adsorbed on the mesoporous titania. The higher the amount of adsorbed acid the higher the decrease of the support surface area. However, the pore size distribution is practically the same.

The FT-IR spectra of titania after being extracted with distilled water did not present any of the characteristic bands of urea, showing that the template was completely removed by water extraction. The spectrum of the  $Ti_{100}$  sample (Fig. 2a) displays bands at 1618 and 3427  $cm^{-1}$  assigned to the OH bending and stretching of water [23] that have been incorporated in the structure of the solid [24]. Also, in

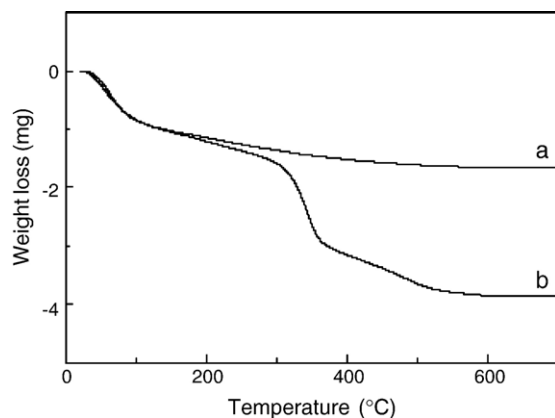


Fig. 1. DTA diagrams of  $Ti_{100}$  (a) and  $TriTi_{100}$  (b) samples.

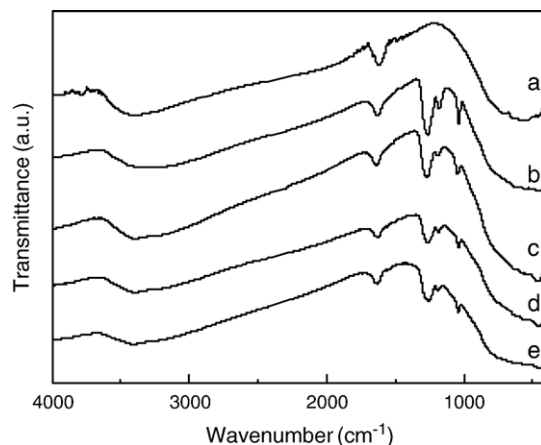


Fig. 2. FT-IR spectra of  $Ti_{100}$  (a),  $TriTi_{100}$  (b),  $TriTi_{200}$  (c),  $TriTi_{300}$  (d), and  $TriTi_{400}$  (e) samples.

the energy interval below 800  $cm^{-1}$ , the band due to stretching vibration  $Ti-O$  is observed.

FT-IR spectra of  $Ti_{200}$ ,  $Ti_{300}$ , and  $Ti_{400}$  showed features similar to those observed for the  $Ti_{100}$  sample, but the intensities of the bands at 1618 and 3427 decreased when the calcination temperature increased, in parallel with the reduction of the  $S_{BET}$ .

The FT-IR spectrum of the  $TriTi_{100}$  sample (Fig. 2b) displays bands at 1267, 1183, and 1037  $cm^{-1}$  in addition to those present in the  $Ti_{100}$  sample. The first two bands are due to the  $S=O$  stretching mode of the adsorbed trifluoromethanesulfonic acid and the last one is assigned to the  $C-F$  stretching [25,26]. These bands are also present in the spectra of  $TriTi_{200}$ ,  $TriTi_{300}$ , and  $TriTi_{400}$  catalysts, although their intensities are lower as a result of the lower amount of trifluoromethanesulfonic acid adsorbed on the support.

With regard to the characterization by XRD, the pattern of  $Ti_{100}$  (Fig. 3) exhibits only the characteristic peaks of anatase phase at  $2\theta = 25.3^\circ$  (101),  $37.9^\circ$  (004),  $47.8^\circ$  (200) and  $54.3^\circ$ . The crystallinity of the supports increases when the calcination temperature is raised and the peak at  $54.3^\circ$  splits into two peaks at  $54.0^\circ$  (105) and  $54.9^\circ$  (211) when the temperature is over 200 °C.

The XRD patterns of  $TriTi_{100}$ ,  $TriTi_{200}$ ,  $TriTi_{300}$ , and  $TriTi_{400}$  showed features similar to the corresponding support. Further, the position and intensity of the characteristic peaks of anatase phase

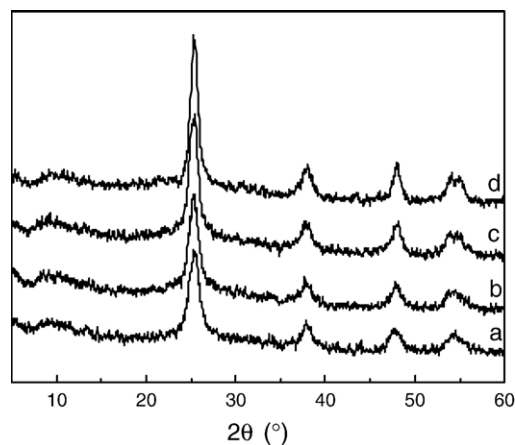


Fig. 3. XRD patterns of  $Ti_{100}$  (a),  $Ti_{200}$  (b),  $Ti_{300}$  (c), and  $Ti_{400}$  (d) samples.

present in the titania used as support did not change after their impregnation with trifluoromethanesulfonic acid.

### 3.2. Acidity measurements

The acidity measurements of the catalysts by means of potentiometric titration with *n*-butylamine allow us to estimate the number of acid sites and their acid strength. As a criterion to interpret the obtained results, it was suggested that the initial electrode potential ( $E_i$ ) indicates the maximum acid strength of the sites, and the value of meq amine/g solid where the plateau is reached indicates the total number of acid sites [27]. Nevertheless, the end point of the titration given by the inflexion point of the curve is a good measure to carry out a comparison of the acidity of the different samples. On the other hand, the acid strength of these sites may be classified according to the following scale [27]:  $E_i > 100$  mV (very strong sites),  $0 < E_i < 100$  mV (strong sites),  $-100 < E_i < 0$  (weak sites) and  $E_i < -100$  mV (very weak sites).

The titration curves of the catalysts are shown in Fig. 4a. According to the previous classification, the samples present very strong acid sites, with  $E_i$  values in the range of 550–700 mV. The number of acid sites determined by potentiometric titration decreases in parallel with the decrease of  $N_{\text{Tri}}$ , the amount of acid firmly adsorbed to the support.

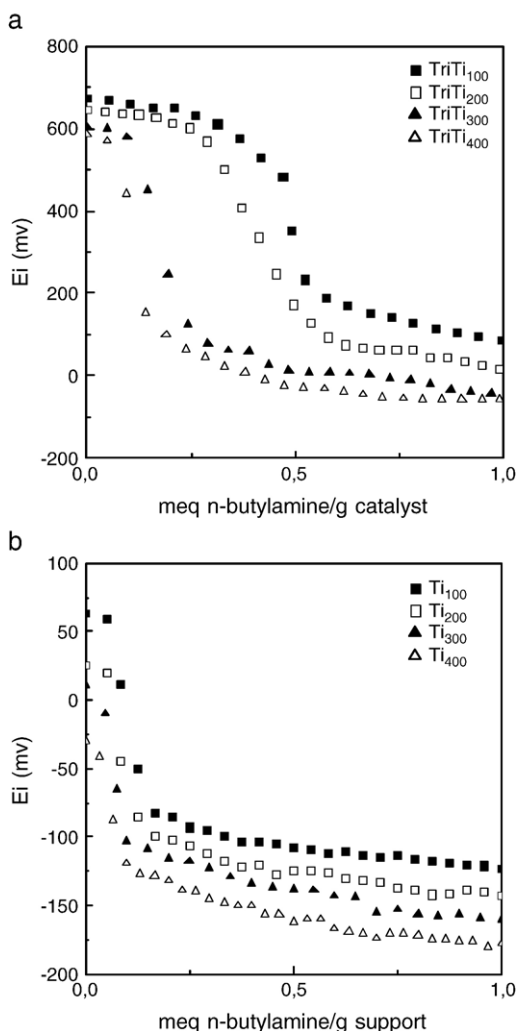


Fig. 4. Potentiometric titration curves of TriTi catalysts (a) and the corresponding supports (b).

Table 2

Specific conversion in isopropanol dehydration and acid strength of trifluoromethanesulfonic acid supported catalysts

Sample	SCV <sub>IPA</sub>	$E_i$ (mV)
TriTi <sub>100</sub>	$1.62 \cdot 10^{-2}$	673
TriTi <sub>200</sub>	$1.12 \cdot 10^{-2}$	647
TriTi <sub>300</sub>	$1.02 \cdot 10^{-2}$	606
TriTi <sub>400</sub>	$0.95 \cdot 10^{-2}$	586

SCV<sub>IPA</sub>: (moles of transformed isopropyl alcohol)/(moles of CF<sub>3</sub>SO<sub>3</sub>H in the catalyst) per second.

Additionally, the acid strength of the catalysts decreases slightly in the same way, probably as a result of the diminution of the support acid strength (Fig. 4b). The support acid strength drops as a result of the partial dehydroxylation that takes place during the thermal treatment of the solids.

The isopropanol dehydration has been used by several authors [28,29] as a test reaction for comparing the acidity of different catalysts. Isopropanol decomposition can form either propene and water (dehydration) or acetone and hydrogen (dehydrogenation). At high temperatures (300–600 °C), rupture of the C–C bonds can occur to give alkanes, CO, and CO<sub>2</sub> [30].

The results of the isopropanol decomposition catalyzed by TriTi<sub>100</sub>, TriTi<sub>200</sub>, TriTi<sub>300</sub>, and TriTi<sub>400</sub> catalysts are shown in Table 2. Under working conditions, it was found that isopropanol decomposes to propene, and only traces of acetone and diisopropylether were detected by means of GCMS. The specific isopropanol conversion (SCV<sub>IPA</sub>) decreases in the following order: TriTi<sub>100</sub> > TriTi<sub>200</sub> > TriTi<sub>300</sub> > TriTi<sub>400</sub>, in parallel with the decrease of the acid strength (Table 2).

The acidic characteristics found through the isopropanol dehydration test reaction are straightly correlated with those found using the potentiometric titration technique.

## 4. Conclusions

Mesoporous titania materials have been prepared using urea as a pore-forming agent, via HCl catalyzed sol–gel reactions and impregnated with trifluoromethanesulfonic acid.

The amount of trifluoromethanesulfonic acid firmly adsorbed on the support depends on the number of –OH groups available on the titania to be protonated, which decreases with the increase in the calcination temperature.

According to the potentiometric titration measurements, the catalysts present very strong acid sites. Their acid strength decreases slightly as a result of the partial dehydroxylation that takes place during the thermal treatment of the supports.

The specific catalytic activity of the catalysts in the isopropanol dehydration test reaction is straightly correlated with the acid strength found using the potentiometric titration technique.

Based on these results, trifluoromethanesulfonic acid supported on mesoporous titania presents suitable properties to be used as solid catalysts, which are very attractive for many processes in replacement of conventional liquid catalysts.

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