



# Trifluoromethanesulfonic acid immobilized on zirconium oxide obtained by the sol–gel method as catalyst in paraben synthesis

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## ABSTRACT

The parabens, alkyl esters of p-hydroxybenzoic acid, were synthesized using trifluoromethanesulfonic acid immobilized on zirconium oxide (zirconia) as catalyst. The oxide was obtained by the sol–gel method, using urea as a pore-forming agent. After removing urea by extraction with water, the solid was dried and then calcined at 100, 205, 310 and 425 °C for 24 h. Afterward, it was impregnated with trifluoromethanesulfonic acid in toluene at reflux and leached to remove the weakly adsorbed acid. Mesoporous materials were obtained, whose mean pore diameter increased with the temperature of the thermal treatment of the support, while the specific surface area and the amount of acid bonded to the support decreased. The samples are crystalline from 400 °C and are thermally stable up to 250 °C. The catalysts have strong acidity and the number of acid sites decreased with the acid content in the support. The catalytic activity in the synthesis of propyl paraben, expressed as moles of ester formed at 5 h/mol acid in the catalyst, decreased when samples obtained from supports thermally treated at higher temperature were used. The activity also slightly diminished for the synthesis of different parabens in the order propyl > ethyl > methyl ester.

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## 1. Introduction

The parabens are esters of p-hydroxybenzoic acid, which are widely used as preservatives in food and also in cosmetics. They are antimicrobial agents, being more active against fungi and yeast rather than against bacteria.

The esters of p-hydroxybenzoic acid were obtained with the purpose of replacing salicylic and benzoic acids, both of which have the drawback of being effective only in the highly acid pH range, assuming that the esters might be advantageous in this aspect since they have a wide pH range [1]. Recently, excellent reviews have been published about parabens, which deal not only with their properties and uses, but also report toxicological and risk assessment studies [2–4].

The antimicrobial action of p-hydroxybenzoic acid esters increases with the chain length, but the solubility decreases; hence, in practice, the esters with shorter chain length are commonly used.

The parabens are obtained through the reaction of the corresponding alcohol with p-hydroxybenzoic acid, usually catalyzed by acids. Due to the increasing awareness about environmental care, it is advisable to use solid catalysts to avoid the use of mineral acids,

which generate a large amount of acid waste. At the same time, they allow for easy product and catalyst separation, thus decreasing the need of the classical separations by distillation or extraction.

The heterogeneization of trifluoromethanesulfonic acid ( $\text{CF}_3\text{SO}_3\text{H}$ ) by immobilization on a suitable support is an interesting alternative to contribute to the field of clean processes. This acid, also named triflic acid, has a highly acidic nature and an excellent thermal stability; it also has good resistance to reductive and oxidative dissociation, with no generation of fluoride ions [5].

The trifluoromethanesulfonic acid was used as an efficient homogeneous catalyst in many organic reactions, such as polymerization and acylation [6,7], among others, but has environmental disadvantages because the recovery of triflic acid (Tri) from the reaction mixture results in the formation of large amounts of waste.

Papers dealing with Tri heterogeneization are scarce, though its immobilization on zirconium hydroxide for its use in the biphenyl benzoylation reaction [8], and in the synthesis of flavones and chromones immobilized on carbon [9] or titania [10] has been reported.

With the purpose of making a contribution to a little explored field and as a continuation of previous work, the preparation and characterization of new catalysts obtained by impregnation of trifluoromethanesulfonic acid on zirconia prepared by the sol–gel method, using zirconium propoxide as precursor, and urea as a nonsurfactant low-cost pore-forming agent, is reported.

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The effect of the calcination temperature of the support on the physicochemical, acidic and textural characteristics of the catalysts was studied. The catalytic behavior of the prepared materials in paraben synthesis was firstly studied through the esterification of *p*-hydroxybenzoic acid with propyl alcohol in a conventional batch glass reactor at atmospheric pressure. In addition, the efficiency of the obtained catalysts was tested in the esterification of *p*-hydroxybenzoic acid with methanol, ethanol and *n*-propanol in an autoclave reactor at the self-generated pressure. The results are correlated with the catalyst properties.

## 2. Experimental

### 2.1. Support preparation

Zirconium propoxide (Aldrich, 26.6 g) was mixed with absolute ethanol (Merck, 336.1 g) and stirred for 10 min to obtain a homogeneous solution under  $N_2$  at room temperature. Then  $0.47 \text{ cm}^3$  of 0.28 M HCl aqueous solution was dropped slowly into the above mixture to catalyze the sol–gel reaction.

After 3 h, 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 up to dryness. The solid was ground into powder and extracted with distilled water for three periods of 24 h, in a system with continuous stirring, to remove urea. Afterwards, portions of the obtained solid were calcined at 100, 205, 310, or 425 °C for 24 h, thus obtaining the supports identified as  $Zr_{T100}$ ,  $Zr_{T200}$ ,  $Zr_{T300}$ , and  $Zr_{T400}$ , respectively.

### 2.2. Catalyst preparation

Trifluoromethanesulfonic acid (0.01 mol, Alfa Aesar) was added dropwise to a mixture of  $Zr_{TX}$  (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 then extracted with a mixture of dichloromethane and diethyl ether ( $40 \text{ cm}^3/\text{g}$  of solid) for three periods of 4 h in order to remove the acid weakly attached to the support. Afterwards, they were dried again at 100 °C for 24 h. The amount of trifluoromethanesulfonic acid retained in the solids was determined by C and S elemental analysis with a Carlo Erba EA1108. The samples were named  $\text{TriZr}_{T100}$ ,  $\text{TriZr}_{T200}$ ,  $\text{TriZr}_{T300}$ , and  $\text{TriZr}_{T400}$ .

### 2.3. Solid characterization

The characterization of the thermal properties of the supports and the catalysts was performed by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses, with a Shimadzu DT 50 thermal analyzer. The measurements were carried out under argon, with a 25–50 mg sample, and a heating rate of 10 °C/min, using quartz cells as sample holders and  $\alpha\text{-Al}_2\text{O}_3$  as reference.

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

X-ray diffraction (XRD) patterns of the solids were recorded with Philips PW-1732 equipment, using  $\text{Cu K}\alpha$  radiation, Ni filter, 20 mA and 40 kV in the high voltage source, a 5–60°  $2\theta$  scanning angle range, and a scanning rate of 1° per min.

**Table 1**  
Trifluoromethanesulfonic acid amount in the catalysts.

Sample	$N_{\text{Tf}} (\text{mmol CF}_3\text{SO}_3\text{H/g})$	$W_{\text{Tf}} (\text{mmol CF}_3\text{SO}_3\text{H/g})$
$\text{TriZr}_{T100}$	0.91	0.88
$\text{TriZr}_{T200}$	0.53	0.49
$\text{TriZr}_{T300}$	0.41	0.38
$\text{TriZr}_{T400}$	0.10	0.11

Fourier transform infrared (FT-IR) spectra of the samples were recorded using Bruker IFS 66 FT-IR equipment, pellets with approx. 1% w/w of the sample in KBr, in a measuring range of 400–4000  $\text{cm}^{-1}$ .

The acidity of the solids was measured by means of potentiometric titration. A known mass of solid was suspended in acetonitrile and stirred for 3 h. Then, the suspension was titrated with 0.05 N *n*-butylamine in acetonitrile solution at a flow of  $0.05 \text{ cm}^3/\text{min}$ , measuring the electrode potential variation in a digital pH meter Hanna 211 with a double-junction electrode.

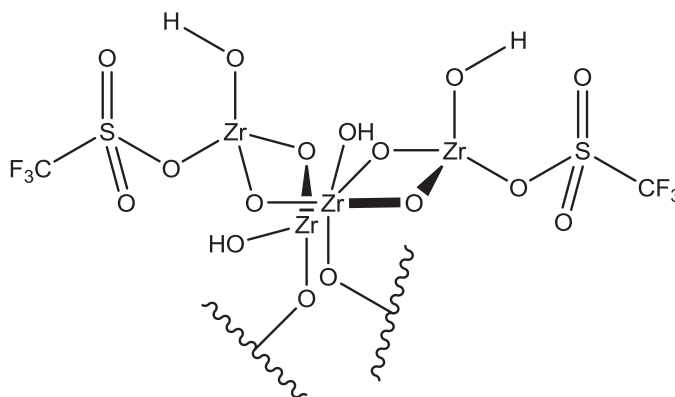
### 2.4. Paraben synthesis

The esterification of *p*-hydroxybenzoic acid with propyl alcohol to obtain propyl paraben was carried out in liquid phase at 100 °C in a 50 ml batch glass reactor equipped with a condenser and a magnetic stirrer. The reagent mixture was heated under stirring and then the catalyst was added. An *n*-propanol:*p*-hydroxybenzoic acid:catalyst molar ratio of 10:1:0.1 was used. Samples were periodically taken and analyzed by gas chromatography in a Shimadzu GC-14B chromatograph with TC detector, and using dodecane as internal standard.

The esterification was also performed in a 15 ml autoclave reactor heated up to 100 °C, at the self-generated pressure, using the same reagent molar ratio mentioned above, not only to evaluate the catalyst performance in this type of reactor for the esterification of *p*-hydroxybenzoic acid with *n*-propanol, but also with ethanol and methanol, in order to obtain propyl, ethyl and methyl parabens. After 5 h under reaction, the analysis of the reaction mixture was performed by gas chromatography.

## 3. Results and discussion

The amount of trifluoromethanesulfonic acid attached to the support ( $N_{\text{Tf}}$ ), calculated from the elemental analysis, decreased with the increment of the thermal treatment temperature of the support (Table 1). This effect may be explained if the interaction between the trifluoromethanesulfonic acid and zirconia is assumed to be of electrostatic type due to proton transfer to the –OH groups on the support surface with subsequent water evolution



**Scheme 1.**

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