Journal of Molecular Catalysis A: Chemical 322 (2010) 106–112

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Study of solid acid catalysis for the hydration of α-pinene

Maria C. Ávila[a], Nora A. Comelli[a], E. Rodríguez-Castellón[c], A. Jiménez-López[c], R. Carrizo Flores[a], E.N. Ponzi[b], M.I. Ponzi[a,*]

[a] INTEQUI (CONICET-UNSL), 25 de Mayo 384, (5730) V. Mercedes, San Luis, Argentina
[b] CINDECA, Calle 47, N° 257, 1900, La Plata, Buenos Aires, Argentina
[c] Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, Málaga, 29071, Spain

ARTICLE INFO

Article history:
Received 21 October 2009
Received in revised form 3 February 2010
Accepted 23 February 2010
Available online 4 March 2010

Keywords:
α-Pinene
Hydration
α-Terpineol
Trichloroacetic acid

ABSTRACT

The hydration of α-pinene using solid acid catalysts was studied. The catalysts were prepared by impregnating trichloroacetic acid (TCA) on different supports such as silica, titania and zirconia (TCA/SiO_2, TCA/TiO_2 and TCA/$ZrO_2 \cdot nH_2O$, respectively). The TCA/TiO_2 catalyst converted α-pinene into hydrocarbons, while the TCA/$ZrO_2 \cdot nH_2O$ catalyst was active and selective for producing alcohols, with a conversion of 57% and a selectivity of 75% of total alcohols, and showed 57% selectivity for α-terpineol. The TCA/SiO_2 sample did not show catalytic activity due to the elimination of the trichloroacetic acid during the preparation step of the catalyst. An additional stability study was performed with the TCA/$ZrO_2 \cdot nH_2O$ sample. The presence of TCA in the different impregnated samples was studied using FT-IR, and the TCA content was determined by thermogravimetric analysis. The surface content of TCA in fresh and used catalysts was studied with XPS, and the textural properties and crystalline structures were analysed by BET and XRD, respectively. Additionally, the nature of the acid centres was characterised by pyridine adsorption coupled with FT-IR, and the acidity was determined by potentiometric titration.

1. Introduction

The hydration of terpenes via acid catalysis is an important method for alcohol synthesis, and has several applications in the perfume and pharmaceutical industries. α-Terpineol, 4-terpineol and terpineol hydrate are, from commercial viewpoints, the most interesting derivatives of α-pinene. α-Terpineol exhibits antimicrobial activity and is used for wound healing and insect bites.

The hydration of α-pinene with acid catalysts leads to a complex mixture of monoterpenes (alcohols and hydrocarbons) [1]. α-Pinene reacts in acidic medium to provide terpenic hydrocarbons by expansion of its ring, forming compounds such as bornanes and fenchones (camphene, fenchene and bornylene), or by opening of the four-carbon ring, forming p-menthanes (limonene, terpinolene and α- and γ-terpinene). When the hydration reaction is carried out in the presence of water with acid catalysts, in addition to the products mentioned above, alcohols such as α-terpineol and borneol are also obtained. α-Terpineol, an important monoterpenic monocyclic alcohol, is industrially obtained through the hydration of α-pinene with an aqueous mineral acid, giving rise to the cis-terpene hydrate, followed by a partial dehydration to α-terpineol [2].

The synthesis of alcohols from α-pinene in the presence of different catalysts has been well studied, and intensely so in the last ten years. Vital and co-workers [3–7] reported the use of solid acid catalysts such as zeolites and impregnated phosphomolybdic acid (HPMo) on polymeric membranes for α-pinene hydration, achieving 100% conversion with selectivities for α-terpineol between 50% and 70%, although it required 150 h of reaction time.

Robles-Dutenhefner et al. [8] used phosphotungstic acid ($HPW_{12}O_{40}$) as a catalyst and mixtures of acetic acid and water for limonene and α-pinene hydration. They studied the reaction under homogeneous and heterogeneous conditions with supported phosphotungstic acid on silica. A conversion of 90% was observed in the homogeneous reactions, with selectivities around 85% for monocyclic and bicyclic alcohols, but the acid had to be recovered from the reaction liquid due to its strong acidity and contamination problems. Experiments with the supported catalyst showed a considerable decrease in conversion and the appearance of a large percentage of isomerisation products. Román-Aguirre et al. [9] used oxalic or chloroacetic acid for the transformation of α-pinene and obtained conversions of 80% with selectivities of 70% for α-terpineol after 4 h, but the dissolved acid had to be separated. Mochida et al. [10] reported the use of zeolites and obtained 100% conversion, but with low selectivity for alcohols (around 57%).

The influence of several acids (HCl, H_2SO_4, and TCA) in the hydration reaction of α-pinene, maintaining a constant acid concentration, was previously studied [11], and it was found that TCA

---

[*] Corresponding author. Tel.: +54 02657430954; fax: +54 02657430980.
E-mail address: mponzi@fices.unsl.edu.ar (M.I. Ponzi).

1381-1169/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2010.02.028

acid was the most selective. For this reason, now we study this acid on different supports.

Heterogeneous catalysis is a cleaner process, where the solid catalyst is easily separated from the reaction mixture. This is an important advantage, although a drawback of homogeneous catalysis is the deposition of decomposition products since the acid is also present.

In this study, relevant results of the hydration of α-pinene using trichloroacetic acid (TCA) supported on SiO_2, TiO_2 and $ZrO_2 \cdot nH_2O$ (TCA/SiO_2, TCA/TiO_2 and $TCA/ZrO_2 \cdot nH_2O$ catalysts) are presented.

2. Experimental

2.1. Catalysts

$ZrO_2 \cdot nH_2O$ was obtained through the hydrolysis of zirconium oxychloride, $ZrOCl_2 \cdot 6H_2O$ (Fluka). The necessary amount of aqueous ammonia (tetrahedron 28%) was added to the zirconium oxychloride to reach a pH of 10. The product obtained by hydrolysis was filtered and washed until no chloride ions remained in the wash water. Finally, the material was dried at 100 °C for 12 h. The SiO_2 (Aerosil 200 Degussa) and TiO_2 (Titanium oxide 99% Aldrich) supports are commercial products.

TCA/SiO_2, TCA/TiO_2 and $TCA/ZrO_2 \cdot nH_2O$ catalysts were prepared by impregnation of the corresponding support with the necessary amount of an aqueous solution of TCA to obtain nominal loadings of 50%, 50% and 15%, respectively. The precursors were prepared by placing the mixture in a rotary evaporator at 100 °C with a rotation speed of 100 rpm under a vacuum of 350 mmHg and evaporating to dryness. The catalysts were obtained after drying the precursors at 110 °C for 10 h. At 110 °C, the precursors of TCA/TiO_2 and $TCA/ZrO_2 \cdot nH_2O$ only exhibited a mass loss of 0.92% and 1.94%, respectively, which corresponded to water loss, while the precursor of TCA/SiO_2 presented a mass loss of 43.73%, so its catalytic activity was not studied.

2.2. Catalytic tests

The catalytic tests were performed in a 200-cm^3 three-necked glass reactor with a refrigerant and a thermocouple. The reactor was submerged in a thermostatic bath with silicone oil and magnetic stirring. In batch experiments, 7.34 mmol of α-pinene, 10 mL of water and 13.6 mL of isopropyl alcohol were first added. After heating to the desired temperature, the catalyst was added. Aliquots were extracted with a micropipette at fixed times and immediately analysed with a GC17 Shimadzu gas chromatographer equipped with an FID and a capillary DB1 column (60 m in length). The temperature of the column was increased from 75 °C to 200 °C at a heating rate of 3 °C/min.

The reaction products were identified by comparing the retention times of terpene standards or using their Kovats index with confirmation by mass spectroscopy. Reaction products with a percentage lower than 1% were neglected.

The conversion (X) and selectivity (S) for the desired products were defined as follows:

$$X = \frac{\text{converted } \alpha\text{-pinene } \%}{\text{initial } \alpha\text{-pinene } \%}, \qquad S = \frac{\text{desired product } \%}{\text{conversion of } \alpha\text{-pinene } \%}$$

2.3. Catalyst characterisation

The surface areas and pore volumes were determined from nitrogen adsorption isotherms measured at −196 °C in a Gemini V2.00 (Micromeritics Instrument Corp.). The TCA content was determined thermogravimetrically with a TGA-50 (Shimadzu) by measuring the mass loss of the catalysts (100–800 °C) and then subtracting the mass loss of the support. The crystalline structure of the catalysts was studied by an X-ray diffraction using a D-Max III (Rigaku) with Cu Kα radiation (λ = 1.5378 Å, 40 kV, 30 mA). The presence of TCA in the catalysts was detected by FT-IR. The total number of acid centres, as well as the acid strength of these sites, was determined by potentiometric titration with *n*-butylamine [12]. The nature of the acid centres (Brönsted and Lewis) of the supported catalysts was studied through the adsorption of pyridine coupled to FT-IR (Perkin-Elmer Spectrum RX1). Self-supported wafers (12 mg/cm^2) were prepared from the finely divided powders. These wafers were impregnated with 2 μL of pyridine. The discs were left in an air flow for 12 h to eliminate the physisorbed pyridine, and then the spectrum was recorded at room temperature. Brönsted and Lewis sites were identified by bands at 1536 cm^{-1} and 1440 cm^{-1}, respectively.

The presence of surface TCA on the catalysts was monitored by X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectra were collected using a PHI 5700 spectrometer (Physical Electronics) with non-monochromatic Mg Kα radiation (300 W, 15 kV, 1253.6 eV) for the analysis of photoelectronic signals of C 1s, O 1s, Cl 2p, Si 2p and Zr 3d with a multi-channel detector. The spectra of the powdered samples were recorded with constant pass energy values of 29.35 eV using an analysis area with a 720-μm diameter. During data processing of the XPS spectra, binding energy values were referenced to the C 1s peak (248.8 eV) from the adventitious contamination layer. The PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss–Lorentz curves in order to more accurately determine the binding energy of the different element core levels. The error in the BE was estimated to be ca. 0.1 eV.

To analyse the adsorption of the reagents (α-pinene and water) on the catalysts, isothermal adsorption experiments were carried out in a thermobalance as described above. The catalyst was heated at 80 °C in a He flow until constant weight. Then, 20 μL of α-pinene or water was injected in the He flow up until constant weight, and the adsorbed amount was determined by the weight difference.

3. Results and discussion

3.1. Characterisation of the catalysts

3.1.1. Trichloroacetic content

The TCA content of the precursors was calculated from the mass loss (100–800 °C) of the precursors and the support. The TCA content of the catalysts was also calculated using the same procedure. The mass loss of each sample and the TCA content are shown in Table 1.

In the case of the precursor $TCA/ZrO_2 \cdot nH_2O$, the TCA content was 15%, which was coincident with the nominal value. The TCA content of the corresponding catalyst was near 10%, indicating that part of the TCA was lost during the drying process.

A TCA content of 26.5% was observed for the TCA/TiO_2 precursor, while the nominal loading was 50%, indicating an important TCA loss during the preparation of the precursor. The TCA content for the corresponding catalyst was 25.0%. Finally, for TCA/SiO_2, the TCA loss

Table 1
TCA contents for precursors and catalysts.

Support	Mass loss (%) (100 °C and 800 °C)			TCA (%)	
	Support	Precursor	Catalyst	Precursor	Catalyst
SiO_2	–	45.67	1.24	–	–
TiO_2	1.89	27.94	25.91	26.5	25.0
$ZrO_2 \cdot nH_2O$	8.01	21.83	17.13	15.0	10.3

Table 2
Textural properties of the supports and catalysts.

Sample	S_{BET} (m^2/g)	Vp (cm^3/g)	Dp (nm)BJH method
TiO_2	41	0.062	6.87
$ZrO_2 \cdot nH_2O$	124	0.071	2.82
TCA/TiO_2	25	0.034	5.61
$TCA/ZrO_2 \cdot nH_2O$	121	0.053	2.85

was 45.67%, with the nominal loading value being 50%, indicating that practically all of the TCA was lost during the preparation of the precursor.

3.1.2. BET surfaces

Table 2 shows the textural properties of the supports and catalysts. The BET surfaces of the catalysts are lower than those of the supports, with an observed decrease of 39% and 3% for TCA/TiO_2 and $TCA/ZrO_2 \cdot nH_2O$, respectively. The BET surface of $TCA/ZrO_2 \cdot nH_2O$ was nearly five times higher than that observed for TCA/TiO_2. The pore volumes of both catalysts were also lower than those of the corresponding supports. In the case of TCA/TiO_2, the pore diameter (Dp) decreased (18%) with respect to that of the support, while an increase of 1% was observed for $TCA/ZrO_2 \cdot nH_2O$. This increase is difficult to justify, and this small difference can be attributed to the low precision of the BJH method in the micropore region. The adsorption isotherms for the support and TCA/TiO_2 are of type III according to IUPAC classification, and their average pore diameters are in the range of mesopores. This type of isotherm occurs when the adsorbate–adsorbent interaction is weak. However, the isotherm for the catalyst $TCA/ZrO_2 \cdot nH_2O$ is of type I. In this type of isotherm, the adsorption takes place at relatively low pressures and is characteristic of microporous solids, although its average pore diameter is slightly larger than 2 nm, the upper limit established by the IUPAC for micropores.

3.1.3. XRD studies

The crystalline structure of the solids was studied by XRD. The powder diffractogram of TCA/TiO_2 showed reflection lines at 17°, 22° and 32°, which were assigned to TCA (JPDC 42.1605), while in the case of $TCA/ZrO_2 \cdot nH_2O$, the diffractogram did not show reflection lines corresponding to TCA. This was attributed to TCA dispersion due to the high surface area of the support.

3.1.4. FT-IR results

The presence of TCA in the catalysts was studied by FT-IR. Fig. 1 shows the spectra of pure TCA, TCA/TiO_2 and $TCA/ZrO_2 \cdot nH_2O$. The spectrum of TCA exhibited diagnostic bands such as those due to carbonyl stretching and carboxylic groups affected by the inductive effect of three chlorine atoms at 1663 cm^{-1}. Bands centred at 1366 cm^{-1} and 1343 cm^{-1} were also observed and assigned to stretching and bending of the hydroxyl group of the carboxylic moiety. The band at 1026 cm^{-1} was assigned as stretching of the C–O system, and the signal at 933 cm^{-1} was assigned to hydroxyl out-of-plane deformation in dimeric systems. Finally, the bands assigned to stretching and bending due to Cl–C bonds were observed at 830 cm^{-1} and 680 cm^{-1}.

The spectra of the catalysts showed the bands of pure TCA with some modifications. The carbonyl group stretching signal appeared at 1661 cm^{-1}. This signal was slightly weakened due to resonance stabilisation and partial complexation with the metal (type I), as described by Deacon and Philips [13]. This fact is based on the bands at 1420 cm^{-1} and 1300 cm^{-1}, corresponding to the C–O stretching frequency, which is in accordance with the existence of a coordinated metallic carboxylate. The difference between the stretching frequencies of the C=O and C–O bonds supports Deacon's model. The bands that appear at low wavenumbers (770–650 cm^{-1}), the regions of deformation and the out-of-plane flexing of the carboxyl group, are absent in the spectra of both catalysts. This strongly supports the model of catalyst–support interaction chosen, where the carboxylate group is anchored to the support through the metallic atom, forming a rigid plane due to chelation of the free hydroxide bonded to zirconium. This chelation increases the Brönsted acidity since the hydrogen bonded to O–Zr is more labile and facilitates the spherical arrangement of α-pinene in the catalytic process. The spectrum of TCA/SiO_2 was also recorded, and bands due to the presence of TCA were not observed due to loss of the acid during the preparation of the precursor.

3.1.5. Acidity by potentiometric titration

Potentiometric titration with *n*-butylamine (BA) is a conventional technique used to determine acidity. This technique determines the maximum acid strength of the surface sites of a catalyst.

It is has been suggested that the initial electrode potential (E_i) indicates the maximum acid strength of the sites and that the value of meq of amine/g solid at which the plateau is reached indicates the total number of acid sites [14,15]. The acid strength of these sites maybe classified according to the following scale [15]: $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites), $-100 < E_i < 0$ mV (weak sites) and $E_i < -100$ mV (very weak sites).

As expected, an increase of the acid strength of TCA/TiO_2 and $TCA/ZrO_2 \cdot nH_2O$ with respect to the supports was observed (see Fig. 2), but the increase was much higher in the case of $TCA/ZrO_2 \cdot nH_2O$ than for TCA/TiO_2. $TCA/ZrO_2 \cdot nH_2O$ presented an

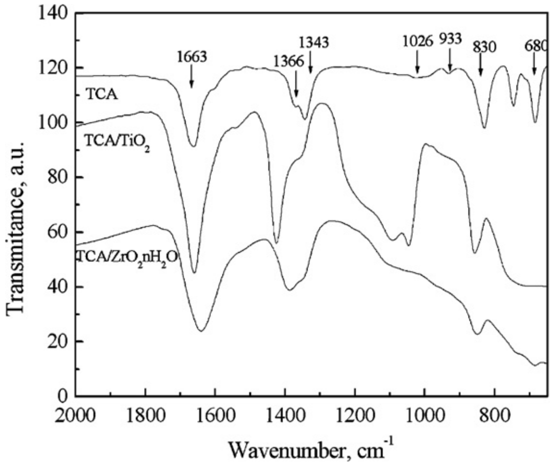

Fig. 1. FT-IR spectra of TCA, TCA/TiO_2 and $TCA/ZrO_2 \cdot nH_2O$.

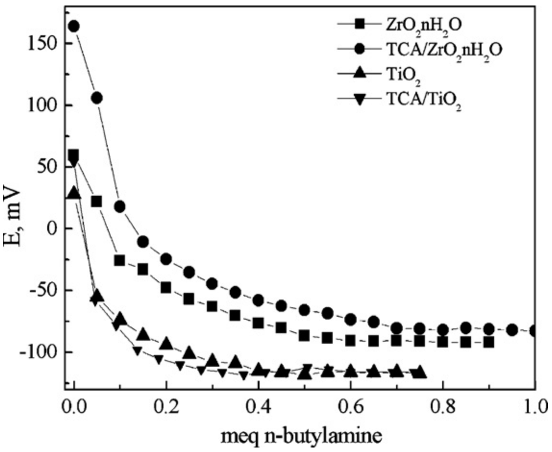

Fig. 2. Potentiometric titration curves for supports and catalysts.

Table 3
Total acidity and concentration of acid sites in the studied supports and catalysts.

Support	*E* (mV)	meq-BA/g cat.	Catalyst	*E* (mV)	meq-BA/g cat.
TiO_2	28.0	0.4	TCA/TiO_2	54.0	0.4
$ZrO_2{\cdot}nH_2O$	59.7	0.6	$TCA/ZrO_2{\cdot}nH_2O$	164	0.8

acid strength higher than 100 mV (164 mV) (see Table 3) and can be considered a very strong acid catalyst, while TCA/TiO_2, TiO_2 and $ZrO_2{\cdot}nH_2O$ have acid strengths lower than 100 mV (54.0 mV, 28.0 mV and 59.7 mV, respectively) and are considered strong acid catalysts. The amount of BA necessary to titrate all of the acidic sites and the shape of the titration curve provide information about the number of sites present. TiO_2 and TCA/TiO_2 required 0.4 meq of BA/g of solid to neutralise all of the sites, while $ZrO_2{\cdot}nH_2O$ and $TCA/ZrO_2{\cdot}nH_2O$ required 0.6 meq and 0.8 meq of BA/g of solid, respectively. Therefore, the latter catalyst was determined to have stronger acidity and to possess a higher number of acid sites.

3.1.6. Acidity by adsorption of pyridine (FT-IR)

The presence of Brönsted and Lewis acid sites was studied using the adsorption of pyridine with monitoring by FT-IR. TiO_2 is a weak acid oxide and presents Lewis acid sites when crystallised as rutile, while $ZrO_2{\cdot}nH_2O$ presents Brönsted and Lewis acidity. The band at 1540 cm^{-1} was assigned to the pyridinium ion formed on a Brönsted acid site, while the band at 1440 cm^{-1} corresponded to the pyridine coordinated to Lewis acid centres. When these supports are impregnated with TCA, their acid properties are modified. TCA/TiO_2 and $TCA/ZrO_2{\cdot}nH_2O$ presented only one band near 1540 cm^{-1} due to the existence of Brönsted acid sites, and bands due to Lewis acid sites were absent.

3.1.7. XPS studies

Surface changes can lead to the deactivation of $TCA/ZrO_2{\cdot}nH_2O$, so fresh and used catalysts were studied by XPS. XPS spectra in the regions of C 1s, O 1s, Cl 2p, Zr 3d and Si 2p were recorded on the fresh catalysts and after one or two runs. Fig. 3 shows the XPS spectra of the regions of C 1s, O 1s, Cl 2p and Zr 3d.

The survey spectra of all samples show the corresponding constituent elements (C, O, Cl and Zr) and Si. This Si signal comes from the presence of SiO_2 (Si 2p at 102.9 eV) due to a surface contamination. The C 1s signal of the fresh catalyst presents several contributions, including a peak at 284.8 eV, characteristic of adventitious carbon, and another at a higher binding energy (288.8 eV) assigned to both carboxylic groups and carbons bonded to three chlorines. The Cl 2p signal is complex and broad due to the presence of at least two types of chlorine. There is a maximum centred at 198.5 eV, which was assigned to the Cl $2p_{3/2}$ peak due to the presence of chlorides, and another maximum at 200.5 eV, assigned to Cl $2p_{3/2}$ due to the covalently bonded chlorine of TCA. This second photoemission is overlapped with the doublet Cl $2p_{1/2}$ of the first emission. The presence of chlorine as chloride could be due to the existence of some unreacted zirconyl chloride. The O 1s signal of the fresh catalyst has a maximum at 530.1 eV, which was assigned to oxygen atoms bonded to zirconium, and a shoulder at 532.3 eV, assigned to oxygen from SiO_2 and oxygen of the carboxylic group. The Zr 3d signal presents a doublet, while the peak corresponding to Zr $3d_{5/2}$ appears at 182.3 eV in the case of the fresh, used and reused catalysts, which corresponds to Zr(IV). The C 1s signal for the used catalysts after the first and second run shows a peak at 288.8 eV due to the presence of surface TCA, but with a lower intensity than that observed in the case of the fresh catalyst. Significant changes were also observed after catalysis in the O 1s signal, where the intensity of the contribution at 532.3 eV decreased with respect to that at 530.1 eV. This is due to a lower surface concentration of TCA, as described above when the C 1s signal was analysed. In the case of the used catalyst after the first run, the shoulder had a lower intensity due to a lower surface concentration of SiO_2. The Cl 2p core level spectra corresponding to the used catalyst after the first and the second runs had the characteristic asymmetry, but the peak at 200.5 eV of TCA was not observed, perhaps due to a lower surface content of TCA and also the overlapping effect of the doublet Cl $2p_{1/2}$ due to chloride.

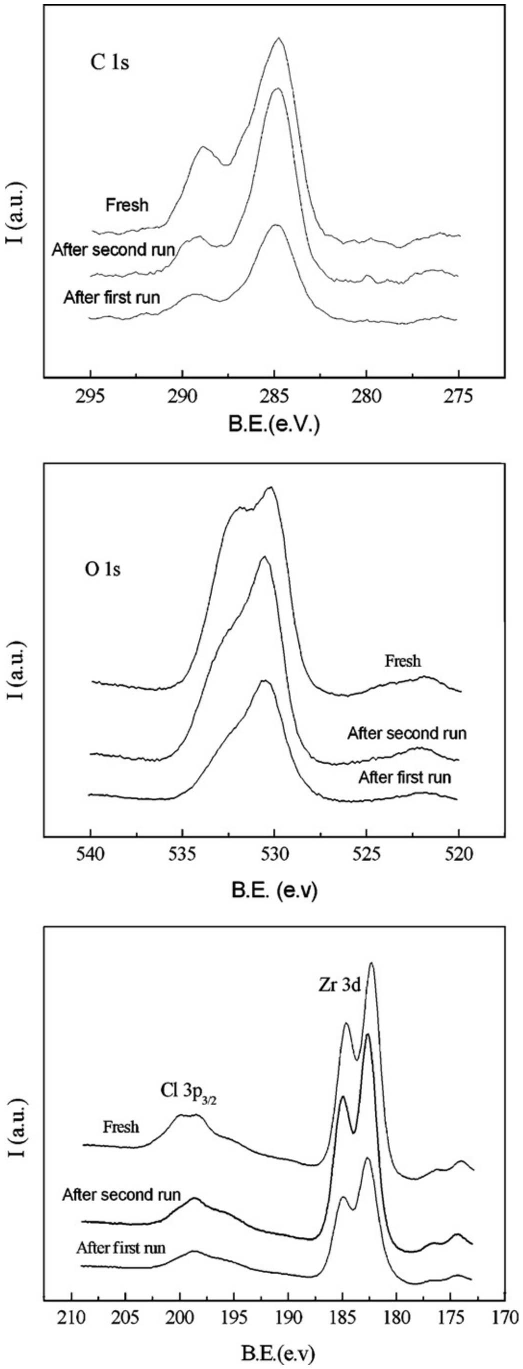

Fig. 3. C 1s,O 1s, Cl 2p and Zr 3d core level spectra for fresh $TCA/ZrO_2{\cdot}nH_2O$ and after one and two runs.

Table 4
Mass ratios determined by XPS for the catalyst TCA/$ZrO_2 \cdot nH_2O$.

Catalyst	Cl/Zr	O/Cl	O/Zr
Fresh	0.25	2.38	0.59
Used after the first run	0.23	1.98	0.46
Used after the second run	0.21	2.36	0.49

Table 5
Hydration of α-pinene over the studied catalysts.

Catalyst	X (%)	X/g TCA	S (%) alcohols	S (%) α-terpineol
TCA/TiO_2	10	0.8	0	0
TCA/$ZrO_2 \cdot nH_2O$	57	3.47	75	57

Reaction conditions: 7.34 mmol α-pinene, 10 mL H_2O, 13.6 mL $(CH_3)_2CHOH$, reaction temperature 80 °C, reaction time 2 h.

Table 6
Adsorption of α-pinene and water at 80 °C.

Catalyst	α-Pinene (wt%)	Water (wt%)
TCA/TiO_2	0.46	0.22
TCA/$ZrO_2 \cdot nH_2O$	2.40	0.35

The mass ratios of Cl/Zr, O/Cl and O/Zr obtained by XPS are shown in Table 4. Although the previous analysis indicated that the surface concentration of TCA decreased after catalysis, the Cl/Zr mass ratio barely decreased, indicating the persistence of surface TCA.

3.2. *Hydration reaction of α-pinene*

α-Pinene in the presence of acid catalysts is attacked by a proton to form a carbocation. This carbocation undergoes a rearrangement or ring opening of its four-carbon ring to generate other carbocations. All of these carbocations can lose a proton and generate monocyclic and bicyclic hydrocarbons or, in the presence of a nucleophile, give rise to monocyclic and bicyclic alcohols (see Fig. 4).

Catalytic studies were performed using TCA/TiO_2 and TCA/$ZrO_2 \cdot nH_2O$. α-Pinene reacts with water in a 1:1 molar ratio to provide monoalcohols. The reaction was carried out in an excess of water with α-pinene as the limiting reagent. Table 5 shows the conversion (X) and selectivity (S) results for both catalysts.

The conversion of α-pinene per mass unit of TCA was about four times lower with TCA/TiO_2, and only isomerisation products were observed under these conditions. However, with TCA/$ZrO_2 \cdot nH_2O$, both hydration and isomerisation products were obtained. As expected, the catalytic activity when using TCA/SiO_2 was non-existent due to the absence of TCA, as indicated by thermoanalysis and FT-IR. The thermogravimetric analysis of TCA/TiO_2 indicated a TCA content of 25 wt%, and its FT-IR spectrum showed bands originating from the presence of TCA. The potentiometric titration results indicated a lower acidity of TCA/TiO_2 with respect to TCA/$ZrO_2 \cdot nH_2O$. The powder DRX patterns for TCA/$ZrO_2 \cdot nH_2O$ did not show reflection lines due to the presence of TCA, probably due to the high dispersion of TCA on this porous support. The textural study of the catalyst indicated a N_2 adsorption isotherm of type I, characteristic of a microporous solid, and a smaller pore size than that observed in the case of TCA/TiO_2. Perhaps due to their different textures, TCA/$ZrO_2 \cdot nH_2O$ leads to hydration products, while TCA/TiO_2 only isomerises α-pinene. Kinetic studies were carried out with the support without TCA, and the results after 3 h of reaction shows a conversion of α-pinene of 20%, yielding products exclusively derived form the isomerisation of α-pinene. Additional experiments were also performed with unsupported TCA. In this case, the observed selectivities are similar to that of the supported catalyst, but with a slightly lower conversion.

Table 6 shows the adsorption of α-pinene and water on TCA/TiO_2 and TCA/$ZrO_2 \cdot nH_2O$ at 80 °C, the reaction temperature.

α-Pinene was adsorbed on TCA/$ZrO_2 \cdot nH_2O$ 5.2 times more than on TCA/TiO_2 and 1.6 times more in the case of water. Interestingly, the observed conversion with TCA/$ZrO_2 \cdot nH_2O$ was 5.7 times higher with respect to that observed with TCA/TiO_2. After 2 h of reaction with TCA/$ZrO_2 \cdot nH_2O$, a conversion of 57% and a selectivity of 57% for α-terpineol were observed. On the basis on these results, a reaction model for the hydration of α-pinene over TCA/$ZrO_2 \cdot nH_2O$ is proposed. Taking into account the origin of the precursors and the crystalline structure of zirconium oxide, Zaitsev [16] proposed three models in accordance with the degree of loss of hydroxyl groups. The precipitation conditions and calcination procedures of zirconia have an influence on the final crystalline form. Yamaguchi [17] proposed three models of the α, β and γ types according to the aging, during which hydroxyl groups are lost. The solid of type γ permits a model that is in agreement with the experimental results to explain anchoring of TCA to the support and the subsequent attack of α-pinene by the acidic hydroxyl groups of hydrated zirconia (Fig. 5) and/or the adsorbed or constituent water molecules.

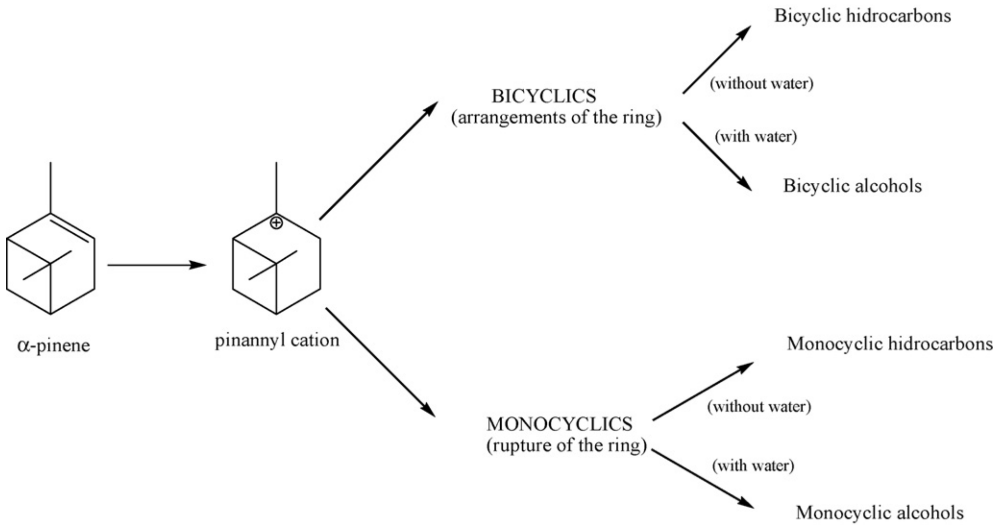

Fig. 4. Hydration reaction scheme of α-pinene.

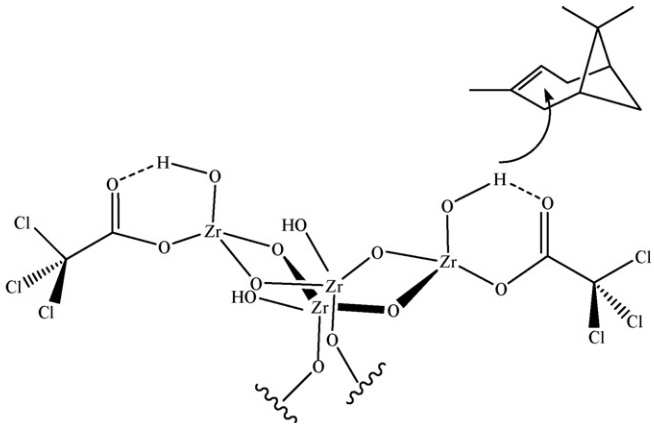

Fig. 5. Model of the interaction of the catalyst with α-pinene.

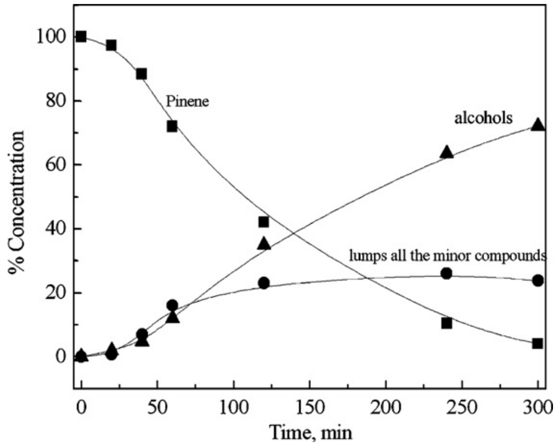

Fig. 6. Concentration of reagents and product over TCA/$ZrO_2 \cdot nH_2O$ vs. time. Reaction conditions: 1.84 mmol α-pinene, 2.5 mL H_2O, 3.4 mL $(CH_3)_2CHOH$, reaction temperature 80 °C, 400 mg TCA/$ZrO_2 \cdot nH_2O$.

Fig. 6 shows the reagents and product profiles obtained with TCA/$ZrO_2 \cdot nH_2O$, including all minor products, in one curve.

At the beginning of the reaction, there is an induction period where α-pinene reacts slowly. After this induction period of 25 min, the production of alcohols increases. A similar behaviour was observed by Castanheiro et al. [7]. The conversion of α-pinene with the reaction time follows a first-order kinetic model, with the interception of the y axis slightly shifted to negative values (Fig. 7). This shift is due to the induction period at low reaction times. The specific speed constant has a value of $1.1 \times 10^2\ \text{min}^{-1}\ g_{cat}{}^{-1}$. van de Waal et al. [3] also demonstrated that the hydration of α-pinene catalysed with zeolites obeys first-order kinetics.

3.3. Stability and reusability of TCA/$ZrO_2 \cdot nH_2O$

Three consecutive catalytic runs were carried out to study the deactivation of the catalyst TCA/$ZrO_2 \cdot nH_2O$. After the first run, the catalyst was separated from the reaction mixture and used in a second and third run with new reagents. Table 7 shows the observed conversion and selectivity values after different reaction times and different runs.

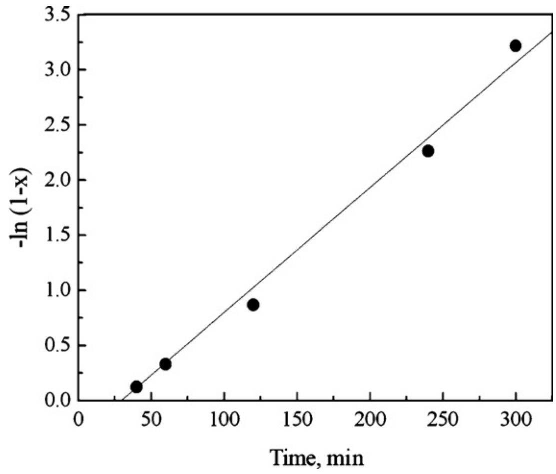

Fig. 7. First-order kinetics for the TCA/$ZrO_2 \cdot nH_2O$ catalyst.

The catalytic activity slightly decreased in the second and third run, while the selectivity for alcohols increased. The XPS results show how the surface Cl/Zr mass ratio was modified after the different runs (see Table 4). The catalytic activity decreased with a decrease of the Cl/Zr mass ratio, while the selectivity followed the opposite trend. Additionally, it was observed that the Cl $2p_{3/2}$ peak at 200.5 eV (covalently bonded chlorine) in the used catalysts disappeared, and the peak Cl $2p_{3/2}$, assigned to chloride (198.5 eV), was maintained.

Some studies to check the stability of the catalyst were performed due to the high solubility of TCA in water. A sample of the catalyst was washed with water and isopropyl alcohol, and then tested in the hydration of α-pinene. The observed results were similar to that found with the unwashed sample. Washed and unwashed

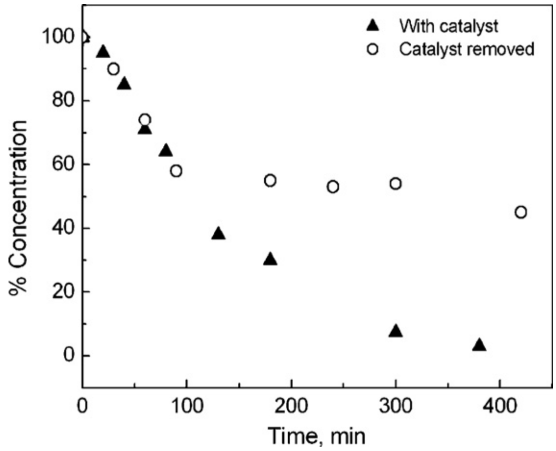

Fig. 8. Variation of the conversion (%) of α-pinene as a function of the reaction time with the catalyst and after separation the catalysts at a conversion of about 60%. Reaction conditions: 1.84 mmol α-pinene, 2.5 mL H_2O, 3.4 mL $(CH_3)_2CHOH$, 80 °C, 400 mg TCA/$ZrO_2 \cdot nH_2O$.

Table 7
Hydration of α-pinene after different runs with the catalyst TCA/$ZrO_2 \cdot nH_2O$.

Time (min)	X (%) first run	X (%) second run	X (%) third run	S (%) alcohols first run	S (%) alcohols second run	S (%) alcohols third run
60	27	20	18	59	73	70
120	57	52	48	75	87	80
300	96	82	77	91	99	95

Reaction conditions: 7.34 mmol α-pinene, 10 mL H_2O, 13.6 mL $(CH_3)_2CHOH$, temperature 80 °C.

samples show similar FTIR spectra indicating that this TCA acid is not leached upon washing. In order to test the stability under the reaction conditions, two separated reactions, under similar experimental conditions, were performed. The first one was carried out up to the presence of a small concentration of α-pinene, while the second one was stopped with a α-pinene concentration of about 60%. The composition of the reaction mixture was analysed up to 420 min of reaction. Fig. 8 shows the conversion (%) of α-pinene as a function of the reaction time in both cases. When the catalyst was separated from the reaction mixture, the reaction is practically stopped. This indicates that TCA acid is not leached, in agreement with the observed results with the reused catalyst.

4. Conclusions

FT-IR studies indicated that the carboxylate group of TCA is anchored to the support through the metallic atom, thereby forming a rigid plane due to possible chelation of the hydroxyl group to Zr to form a six-membered ring. The chelation increases the liability of the proton and consequently the Brönsted acidity. The catalyst TCA/$ZrO_2 \cdot nH_2O$ has a stronger acidity and higher number of acid sites than TCA/TiO_2.

XPS studies indicated that there were two types of chlorines, one from the presence of unreacted zirconyl chloride and a second one belonging to TCA. The former chlorine is more stable after catalysis. The C 1s peak corresponding to the Cl_3–C of TCA of the used catalysts had a lower intensity due to a partial loss of TCA.

The conversion of α-pinene with TCA/$ZrO_2 \cdot nH_2O$ was 5.7-times higher than that observed for TCA/TiO_2. The adsorption of α-pinene over TCA/$ZrO_2 \cdot nH_2O$ was 5.2-times higher than that over TCA/TiO_2. After 2 h of reaction, a conversion of 57% and a selectivity for alcohols of 75% were observed, with 57% selectivity for α-terpineol. The hydration of α-pinene with the catalyst follows first-order kinetics.

In the case of TCA/$ZrO_2 \cdot nH_2O$, used and reused catalysts exhibited lower catalytic activities, but higher selectivities for alcohols. The decrease in catalytic activity is related to a decrease in the Cl/Zr mass ratio on the surface of the catalyst.

Acknowledgements

We acknowledge financial support from CONICET, ANPCyT, UNSL, UNLP and Junta de Andalucía (Excellence Project P06-FQM-01661).

References

[1] R.M. Traynor, R.M. Albert, R.L. Webb, in: D.F. Zinkel, J. Russels (Eds.), Naval Stores, Pulp Chemical Association, New York, 1989, p. 479.

[2] K. Bauer, D. Garbe, Common Fragrance and Flavor Materials, Preparation, Properties and Uses, VCH, Weinhein, 1985.

[3] J. van de Waal, H. van Bekkum, J. Vital, J. Mol. Catal. A 105 (1996) 185.

[4] J. Vital, A.M. Ramos, I.F. Silva, H. Valente, J.E. Castanheiro, Catal. Today 56 (2000) 167.

[5] J. Vital, A.M. Ramos, I.F. Silva, J.E. Castanheiro, Catal. Today 67 (2001) 217.

[6] J.E. Castanheiro, A.M. Ramos, I. Fonseca, J. Vital, Catal. Today 82 (2003) 187.

[7] J.E. Castanheiro, I.M. Fonseca, A.M. Ramos, R. Oliveira, J. Vital, Catal. Today 104 (2005) 296.

[8] P.A. Robles-Dutenhefner, A. Kelly, M. da Silva, H. Rafiq, Siddiqui, V. Ivan, Kozhevnikov, V. Elena, Gusevskaya, J. Mol. Catal. A 175 (1–2) (2001) 33.

[9] M. Román-Aguirre, L. De la Torre-Sáenz, W. Antúnez Flores, A. Robau-Sanchez, A. Aguilar Elguezabal, Catal. Today 107–108 (2005) 310.

[10] T. Mochida, R. Ohnishi, N. Horita, Y. Kamiya, T. Okuhara, Micropor. Mesopor. Mater. 101 (2007) 176.

[11] M.C. Avila, N. Comelli, E.N. Ponzi, M.I. Ponzi, XXI Simposio Ibero-Americano de Catálisis, Málaga, España, 2008.

[12] R. Ruby, G. Pechi, Appl. Catal. A: Gen. 14 (1985) 15.

[13] G.B. Deacon, R.J. Philips, Coord. Chem. Rev. 33 (1980) 227.

[14] D. Bernardi, G. Romanelli, J. Autino, L. Pizzio, Appl. Catal. A: Gen. 324 (2007) 62.

[15] E.A. El-Sharkawy, A.S. Khder, A.J. Ahmed, Micropor. Mesopor. Mater. 102 (2007) 128.

[16] L.M. Zaitsev, Zh. Neorg. Khim. 11 (1966) 1684.

[17] T. Yamaguchi, Catal. Today 20 (1994) 199.