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α-Pinene isomerization to camphene
Effect of thermal treatment on sulfated zirconia

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Abstract

The isomerization reaction of α-pinene produces bicyclic and monocyclic compounds and other products. The purpose of this study is to investigate the influence of the pre-treatment temperature of the catalyst on the concentration of Lewis and Brönsted acid sites and the activity and selectivity of the catalyst. Catalyzed reactions in heterogeneous and homogeneous phases were performed. In heterogeneous reaction, sulfated zirconia (SZ) and pre-treated SZ catalyst at several temperatures were used. The thermal treatment affects the ratio between Brönsted and Lewis sites. Results were contrasted with those obtained with SZ catalyst without thermal treatment. In homogeneous reaction the catalyst is sulfuric acid, and in the reaction medium Brönsted sites are only present coming from the H^+ of the acid. The ratio between bi/monocyclic compounds for H_2SO_4, SZ catalyst and pre-treated catalyst at several temperatures, SZ250, SZ350 and SZ500, varies between 0.4 and 4.3. It can be observed that there exists an optimal thermal treatment where the ratio is higher. FT-IR spectra of adsorbed pyridine on catalysts pre-treated thermally show the presence of Lewis and Brönsted acid sites. The amount of acid sites was determined by TPD of adsorbed pyridine.

Keywords: α-Pinene isomerization; Sulfated zirconia; Camphene

1. Introduction

The α-pinene isomerization in presence of acid catalysts occurs by a mechanism in parallel, where, on one hand bicyclic compounds are obtained as camphene, tricyclene, bornylene through a cycle rearrangement, and on the other hand monocyclic compounds as limonene, terpinolene, α- and γ-terpinene are obtained by means of the rupture of one of the rings (Scheme 1). The isomerization reaction is developed in presence of strong acid catalysts, where the catalyst acidity has a strong effect on the activity and the camphene yield. Camphene is used in the manufacture of camphor and its related compounds.

Zeolites, clays, and different oxides have been used in this reaction [1–14]. Our group reported previously the α-pinene isomerization on catalysts of sulfated zirconia and sulfated zirconia modified with the addition of Fe and Mn, zirconia with molybdate and zirconia with wolframate, kaolinitic and bentonitic clays [15–18].

In the isomerization of α-pinene the activity is associated with the catalyst acidity while the type of active sites (Brönsted or Lewis) and their strength affect the selectivity to bicyclic and monocyclic products.

Severino et al. [2] studied the α-pinene isomerization reaction catalyzed with zeolites, and they state that Lewis acid sites (weaker than Brönsted sites) are beneficial for the formation of bicyclic compounds, while Brönsted sites are the responsible for the formation of monocyclic compounds.

Yadav et al. [13] studied the reaction catalyzed by a montmorillonite pre-treated with sulfuric acid. They reported α-pinene conversions of 96% with selectivity for camphene ranging from 39 to 49%. The production of monoterpenes is related with the concentration of sulfuric acid, thus, concentrations between 1 and 4N produce principally limonene, while concentrations between 5 and 9N produce α-terpinene. The highest conversions and selectivities in camphene were obtained at 150 °C.

De Stefanis et al. [1] compared the α-pinene isomerization in mesoporous solids and found that the reaction is influenced by the solid acidity more than by the accessibility of reagents to the pores.

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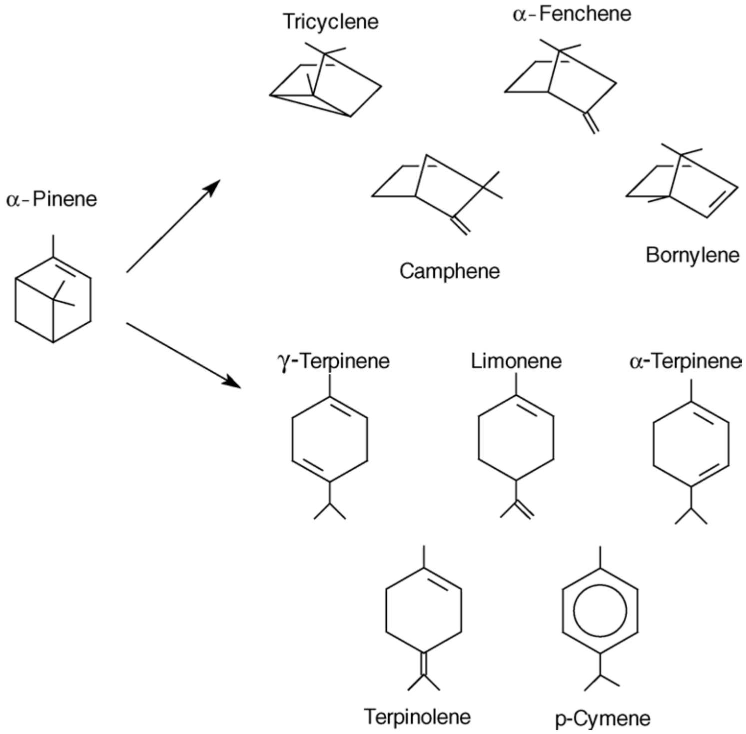


Scheme 1. Involved compounds in the α-pinene isomerization.

Encormier et al. [11] studied the catalyzed reaction by sulfated zirconia and found that at low S loads, weak acid sites are formed favoring the camphene formation while that at high loads, strong acid sites are formed favoring the limonene formation.

Although it is clear that weak acid sites direct the reaction toward the camphene obtention and strong acid sites direct the reaction toward the limonene formation, there exists controversy about the site type that influences on the catalyst activity. Sulfated zirconia has been widely studied since it is able to catalyze the isomerization of alkenes of short lineal chain at temperatures relatively low. The sulfated zirconia is very sensitive to preparation conditions and to the activation process used before reaction. The activation temperature plays a very important role in the acidity determination of the catalyst due to its hygroscopic properties and influences on the reaction selectivity.

Studies performed by different authors Hammache and Goodwin Jr. [19], Gonzalez et al. [20] show that the Brönsted/Lewis acid site ratio (B/L) decreased with the increase in drying temperature as the Brönsted acid sites were converted to Lewis acid sites upon dehydration.

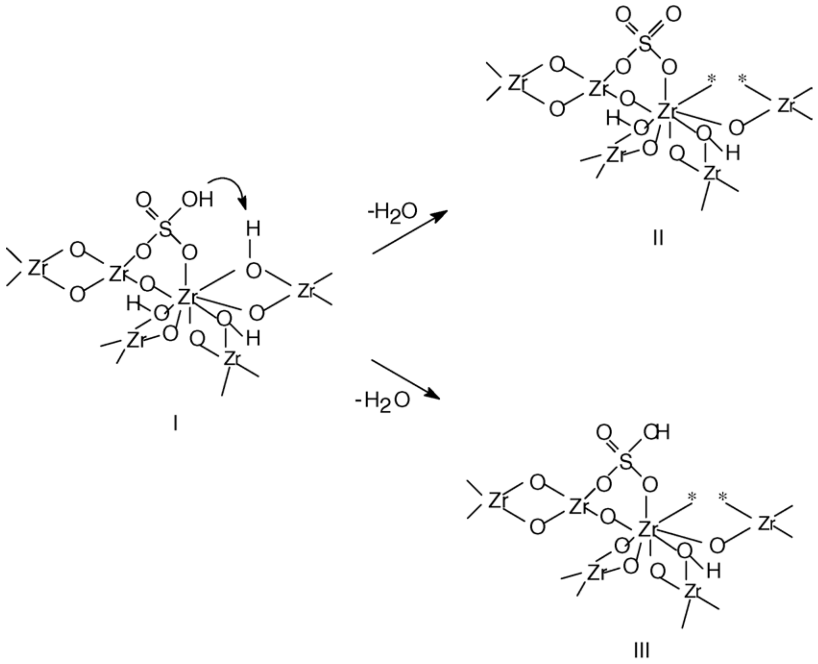
Although several works using sulfated zirconia in different reactions have been published, the role of active sites is not even clear. Several intents have been carried out in order to try to establish models that explain the behavior of these catalysts.

The model of Morterra et al. [21] describes the formation of Lewis sites produced by the highly covalent character of the sulfate ion and the formation of the Brönsted acidity as consequence of the interaction of water molecules with these sulfates.

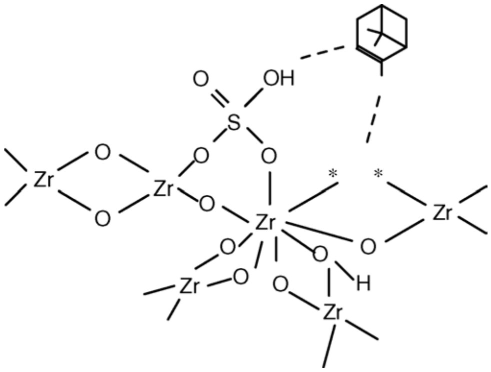
Arata and Hino [22] propose a structure where the sulfate is bonded to two zirconium atoms and suppose that the Brönsted acidity is produced by the attack of water molecules that behave as weak base on Lewis acid sites.

Clearfield et al. [23] propose a model (Scheme 2) based on the supposition that the dominant species is the bisulfate ion when the catalyst is prepared with sulfuric acid, thus forming the species I. The bisulfate ion can react by heating with an adjacent hydroxyl group generating Lewis acid sites, species II, or the water is freed from two neighbor hydroxyl groups maintaining intact the bisulfate ion structure, species III, and then generating Brönsted acidity. This acidity is produced by the fact that Lewis sites neighbor to the S–O–H group strongly attract electrons, weakening the union and facilitating the loss of a H^+ (Scheme 3).

Babou et al. [24] suppose the existence of three types of sites, L_1 assigned to Zr^{4+} atoms of zirconia support, L_2 and B that are related with the adsorbed sulfate species on the surface. By means of outgasing at increasing temperatures, they find that L_1 and B sites decrease with the temperature increase, while L_2 suffer little variation with respect to the same treatment, thus concluding that these last ones are the strongest ones. These authors propose that there exist different sulfate species adsorbed on the surface, generating different types of sites, thus (SO_3)ads generates L_2 sites while (H_2SO_4)ads, $(-HSO_4)$ads and (H_3O^+)ads generate Brönsted sites. The two first Brönsted sites are converted into Lewis L_2 sites by means of the thermal treatment. Hammache and Goodwin Jr. [19], Comelli et al. [25] found that sulfated zirconia presents a maximum activity in the *n*-butane isomerization reaction when it is pre-treated between 500 and 520 °C.



Scheme 2. Model proposed by Clearfield et al. [23].



Scheme 3. Proposed mechanism for α-pinene isomerization.

Our previous studies using sulfated zirconia [17] have provided good results, and for this reason, in the present work, the influence of the thermal treatment of sulfated zirconia on the activity and selectivity in the α-pinene isomerization is studied.

In order to find optimum operation conditions for the camphene formation, the sulfated zirconia catalyst was pre-treated at different experimental conditions, calcined at 600 °C and rehydrated for 24 h (SZ) and then exposed to different thermal treatments 250, 350 and 500 °C (SZ250, SZ350 SZ500).

2. Experimental

2.1. Catalyst preparation

The zirconium hydroxide was obtained by hydrolysis of zirconium oxychloride, $ZrOCl_2 \cdot 6H_2O$ Fluka). The necessary amount of ammonium hydroxide (Tetrahedron 28%) was added to the zirconium oxychloride to reach a pH 10. The product obtained by hydrolysis was filtered and washed up to the non-identification of the ion chloride in the washing water, and finally the material was dried at 120 °C for 12 h.

The precursor with 15% of sulfuric acid was prepared with zirconium hydroxide and the necessary amount of a solution of H_2SO_4 (Merck, 1N) in methanol (Carlo Erba) in a rotary evaporator. The catalyst was obtained by precursor calcination at 600 °C for 4 h and rehydration for 24 h.

In order to analyze the effect of pre-treatment of the catalyst on the activity, the SZ catalyst was treated in muffle for 2 h at 250, 350 and 550 °C and they are denominated as SZ250, SZ350 and SZ500, respectively.

2.2. Catalytic test

The reaction was performed in a glass reactor with three openings; in one of them a reflux condenser is added. The other ones are used for the extraction of the sample, extracted out by a micropipette, and for a thermocouple that measures the reaction temperature. The reactor was heated by a thermostatic glycerin bath. The α-pinene and catalyst were maintained in suspension by means of magnetic stirring at 500 rpm. In a typical run, 5 ml of α-pinene 98.7% purity (provided by Derivados San Luis company) were placed in the reactor and heated up to 120 °C, then, 75 mg catalyst were added and the reaction time started to be registered. A sample of 100 μl was extracted periodically and the analysis was immediately performed. The analysis of the reaction components was carried out in a gas chromatograph equipped with a capillary column DB1 of 60 m and the temperature was increased from 75 up to 200 °C at a rate 3 °C/min. The identification of the products was made by comparison of retention times with pure terpenes and confirmed by mass spectroscopy.

2.3. Characterization

The surface area of the catalyst was determined by using the BET method, in a Micromeritics Accusorb 2100E equipment. The crystalline structure of catalysts was determined by X-ray diffraction studies (XRD) on a Rigaku D-Max III equipment with Cu Kα radiation (λ = 1.5378 Å, 40 kV, 30 mA).

The acidity was determined with TPD experiments of pyridine in a thermobalance Shimadzu model TGA 50. The SZ catalyst was pre-treated at 100, 250, 350 or 500 °C, and cooled up to 35 °C, then, 2 μl of pyridine were added. The temperature was increased up to 100 °C and was maintained for 1 h to eliminate the pyridine physically adsorbed, then, the temperature was increased up to 600 °C with a rate of 10 °C/min.

The nature of the acid sites (Brönsted and Lewis) of the catalyst SZ, SZ100, SZ250, SZ350 and SZ500 was characterized by in situ FT-IR (Perkin-Elmer Spectrum RX1) spectroscopy with chemisorbed pyridine. All the catalyst samples were exposed to a standard thermal treatment involving heat treatment at 25, 100, 250, 350 and 500 °C in a Pyrex glass cell, with KBr windows coupled to a vacuum line. FT-IR studies were carried out at room temperature and pyridine was adsorbed at the partial pressure of pyridine at 25 °C. The pyridine excess was eliminated with vacuum during 1 h at room temperature. Wafer was prepared by using KBr disk technique (5 mg of catalyst/50 mg KBr). The Brönsted/Lewis (B/L) site ratio was calculated from the IR absorbance intensities of bands at 1536 and 1440 cm^{-1}.

3. Experimental results

3.1. Reaction study

The isomerization reaction was studied in heterogeneous phase by the incorporation of sulfated zirconia as a catalyst or in homogeneous phase by the addition of sulfuric acid to α-pinene. In the homogeneous reaction, only Brönsted acid sites are present while in the heterogeneous reaction, the catalysts contain Lewis and Brönsted sites.

Typical kinetic curves for SZ catalyst are presented in Fig. 1a and b, the α-pinene concentration (wt.%) decreases with the time, and the principal reaction product is the camphene, with a production of about 50% after two reaction hours. Limonene and tricyclene follow in production order although in lesser proportion. The other reaction products are obtained in concentrations lower than 4 wt.%.

Conversion of α-pinene and selectivity to any product were determined in the following ways:

$$\text{Conversion}\,(X) = \frac{\text{moles of isomerized}\,\alpha\text{-pinene}}{\text{moles of initial}\,\alpha\text{-pinene}}$$

$$\text{Selectivity}\,(S) = \frac{\text{moles of product}}{\text{moles of isomerized}\,\alpha\text{-pinene}}$$

Table 1 presents α-pinene conversion values (%X) and selectivities to camphene, bicyclic and monocyclic compounds, for the different treatments performed. For the SZ catalyst the selectivity to camphene remains practically constant and is about 58%. The selectivity to bicyclic and monocyclic compounds is 72 and 24% respectively and the ratio between bi/monocyclic compounds is about 3.

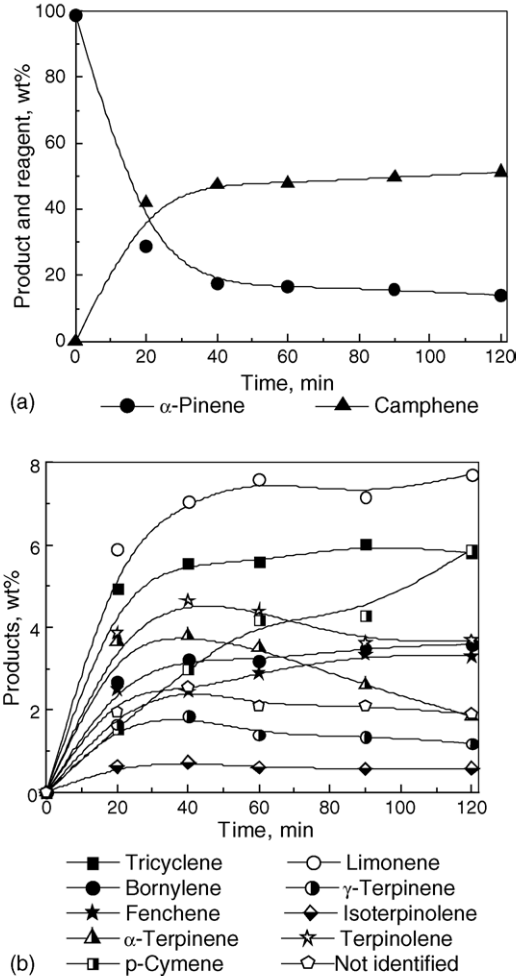


Fig. 1. (a) Concentration of camphene and α-pinene as a function of the reaction time for SZ catalyst. Five milliliters α-pinene, 120 °C, 75 mg catalyst. (b) Product distribution as a function of the reaction time during the isomerization of the α-pinene for SZ catalyst. Five milliliters α-pinene, 120 °C, 75 mg catalyst.

With the SZ250 catalyst, the conversion showed a slight increment, the selectivity to camphene increased almost 10% and the ratio of bi/monocyclic compounds also increased, taking an average value of 4.3.

When the catalyst is exposed to a more severe thermal treatment, SZ350 and SZ500, the conversion decreases, the selectivity to camphene does not evidence any change. The ratio bi/monocyclic compounds decreased to average values of 3.2 and 3.5, respectively.

Activity results as a function of the thermal treatment showed a maximum activity for the catalyst SZ250.

Experiments using sulfuric acid as catalyst were carried out (Table 1), with the same acid load as the one of the SZ catalyst in order to observe the reaction behavior only with Brönsted acid sites. In this case catalytic activity is observed, with a clear decrease in the ratio of selectivities between bicyclic and monocyclic compounds, with relation to values obtained with the SZ catalyst.

Table 1
Conversion and selectivity as a function of the reaction time, of catalysts with different thermal treatment

Catalyst	Time (min)	%X	%S camphene	%S bicyclic	%S monocyclic	Bicyclic/monocyclic
SZ	20	70.8	58.4	72.5	24.1	3.0
	40	82.2	57.1	70.6	25.3	2.8
	60	83.3	56.9	70.8	25.7	2.8
	90	84.1	58.3	73.4	23.0	3.2
	120	85.8	58.9	73.2	24.1	3.0
SZ250	20	73.7	64.8	78.9	18.4	4.3
	40	83.5	65.5	79.0	18.5	4.3
	60	86.7	65.6	78.7	18.9	4.2
	90	87.8	66.0	78.9	18.6	4.2
	120	88.2	67.4	80.4	17.2	4.7
SZ350	20	56.4	58.8	73.2	21.1	3.5
	40	64.8	56.2	69.0	23.6	2.9
	60	68.1	57.3	71.3	21.5	3.3
	90	73.5	57.0	71.4	21.9	3.3
	120	78.4	56.8	68.8	22.7	3.0
SZ500	20	31.9	59.2	74.0	22.7	3.3
	40	42.8	57.8	72.4	20.9	3.5
	60	46.9	58.1	72.7	20.9	3.5
	90	51.9	58.9	74.0	19.6	3.8
	120	56.5	59.3	74.1	20.6	3.6
H_2SO_4	60	5.9	16.8	25.9	74.6	0.4
	90	9.5	15.0	21.3	73.2	0.3
	120	1.4	12.0	16.9	74.4	0.2

Reaction condition: 120 °C and 1.5% catalyst.

The activity measure was also performed by using a ZrO_2 (Z) sample without impregnation with sulfuric acid, in which only Lewis acid sites were found and resulted to be inactive. The catalyst calcined at 600 °C and without rehydration resulted to be also inactive.

If only Lewis acid sites are present (zirconia, Z) the catalyst is inactive, while if only Brönsted acid sites are present (catalyzed with H_2SO_4) there is scarce activity. When both sites are present (sulfated zirconia, SZ), the activity is higher.

3.2. Characterization

The zirconium oxide (ZrO_2) presents low specific surface area, but it is known that the H_2SO_4 addition increases its surface. The surface area for SZ catalyst and pre-treated catalyst at several temperatures, SZ250, SZ350 and SZ500 is 84, 100, 115 and 130 m^2/g, respectively.

From the X-ray diffraction spectrum, the presence of tetragonal phase ($2\theta = 30.2$) and of monoclinic phase is observed ($2\theta = 8.3$ and 31.6); the signals of the tetragonal phase are more pronounced.

TPD-pyridine results are summarized in Table 2. Weak-medium and strong acidity were estimated by the change of weight of pyridine desorbed in the intervals 100–400 and 400–500 °C, respectively.

There is a decrease in the weak-medium acidity with the increase of pre-treatment temperature:

$$SZ > SZ250 > SZ > 350 = SZ500$$

Also the strong acidity decreases in the same order, but the ratio weak-medium/strong acidity shows a maximum for SZ250.

The type of acid sites (Brönsted or Lewis) presented by the catalyst was studied with FT-IR spectroscopy of chemisorbed pyridine. The adsorption of pyridine on Brönsted acid sites forms a pyridinium ion with IR bands at 1638, 1611, 1540 and 1486 cm^{-1}, whereas pyridine covalently bonded to Lewis acid sites gives characteristic bands at 1486 and 1445 cm^{-1}.

The Brönsted/Lewis (B/L) site ratio was calculated from the IR absorbance intensities of bands at 1536, 1442 cm^{-1}, respectively, and it is shown in Fig. 2.

The Brönsted acidity increases with the pre-treatment temperature up to 100 °C and decreases at higher pre-treatment temperature. The Brönsted acidity increase between the rehydrated and the pre-treated catalyst at 100 °C can be attributed to the presence of water molecules that impede the pyridine adsorption in the SZ catalyst. In the FT-IR spectrum of adsorbed pyridine in the SZ catalyst, a wide band is observed at 1625 cm^{-1} corresponding to the water molecules, this band disappears for the pre-treated catalyst at 100 °C (Fig. 3). The Lewis acidity is

Table 2
Acid strength distribution

Catalysts	Weak-medium acid sites (mg)	Strong acid sites (mg)	Weak-medium/ strong acid sites
SZ	0.177	0.063	2.80
SZ250	0.160	0.040	4.00
SZ350	0.137	0.043	3.20
SZ500	0.135	0.035	3.85

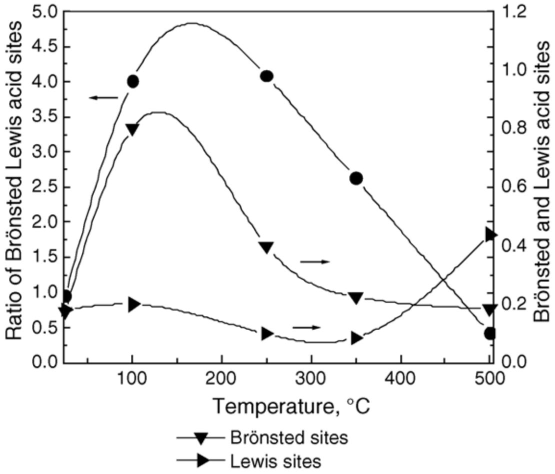


Fig. 2. FT-IR spectra of pre-treated catalysts.

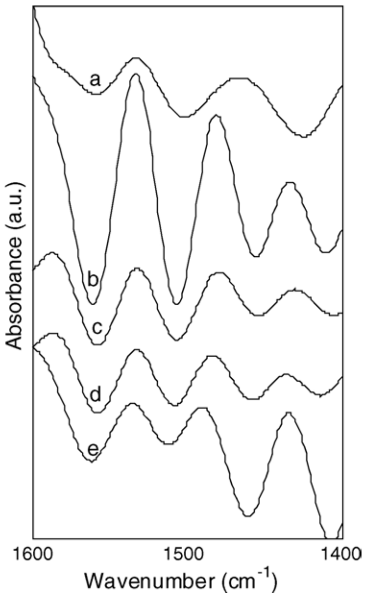


Fig. 3. Absorbance intensity of FT-IR spectra of pyridine adsorbed on SZ and pre-treated catalysts: (a) SZ, (b) 100 °C, (c) 250 °C, (d) 350 °C, and (e) 500 °C.

not substantially modified with the pre-treatment up to 350 °C, but at higher temperature, the Lewis acidity increase is important. The ratio between Brönsted and Lewis acid sites (B/L) passes through a maximum between 100 and 250 °C.

4. Discussion

The sulfated zirconia (SZ) presents on its surface Lewis and Brönsted acid sites and they are very susceptible to the thermal treatment. When the temperature increases the water loss transforms Brönsted acid sites into Lewis acid sites.

When the reaction was carried out with sulfated zirconia calcined at 600 °C and non-rehydrated reaction products were not obtained, it resulted to be completely inactive. With this thermal treatment, some authors state that the Brönsted acidity is completely lost, while Morterra [21] finds that with a treatment at 600 °C, a small amount of Brönsted acidity remains. TPD-pyridine results (Table 2) show that the acidity decreases with the temperature increase.

The Clearfield model proposes that both sites Lewis and Brönsted are present in the sulfated zirconia. The calcination of sulfated zirconia generates on one hand the species III that presents acid Lewis and strong Brönsted sites coming from the weakening of the S–O–H bond, and on the other hand the species II that presents Lewis and weak Brönsted sites coming from OH groups that join two zirconium atoms. This model allows to explain the role of each site in the activity and selectivity of the reaction under study. Thus, the α-pinene molecule is coordinated on Lewis acid sites through the double bond electron-rich, so the molecule is oriented with the gem dimethyl groups as far as possible from the surface and through Brönsted sites a H^+ addition is produced in the double bond. This molecule orientation interacting with the surface favors the formation of camphene, Wystrach [26]. In the absence of Lewis sites, the molecule is not oriented and can reach to the surface with gem dimethyl groups forward and the attack of the ring of four carbons is produced appearing preferably limonene.

According to Babou et al. model [24], at thermal treatment lower than 200 °C, L_1 sites (weak Lewis) and B sites assigned to species H_2SO_4, $-HSO_4$ and H_3O^+ are present, when the catalyst is pre-treated at a temperature higher than 200 °C, species H_2SO_4, $-HSO_4$ are transformed into SO_3 that coordinate with the surface generating strong Lewis sites, L_2. Taking into account this model, the activity in the α-pinene isomerization reaction could increase slightly with thermal treatments up to 200 °C by the transformation of these Brönsted sites and the appearance of Lewis sites, that according to our understanding are the responsible for anchoring the molecule near the surface so that then it is attacked by a Brönsted site. Treatments at higher temperatures eliminate Brönsted sites and for this reason the activity decreases. This model could also explain the maximum observed in the ratio between bicyclic and monocyclic compounds, with the catalyst pre-treated at 250 °C, supposing that at those temperatures the better ratio between Lewis and Brönsted sites is obtained to orient the molecule and produce the attack. At higher thermal treatment temperature, L_2 sites are strong and favor the attack of the ring of four carbons generating limonene and also compounds of high molecular weight with retention times higher than the one of terpinolene.

The acidity generated by the sulfuric acid in homogeneous phase, strong Brönsted acidity, makes the reaction to be active, but as there is no orientation in α-pinene molecules, they are attacked preferably in the ring of four carbons forming monocyclic compounds.

5. Conclusions

If only Lewis acid sites are present (zirconia, Z) there is no activity, while if only Brönsted acid sites are present (catalyzed with H_2SO_4) there is scarce activity. When both sites are present (sulfated zirconia, SZ), the activity is higher.

The treatment temperature has an important effect on the reaction activity but it has not a drastic effect on the selectivity to camphene. The activity and the ratio between bicyclic and monocyclic compounds present a maximum for the SZ250 catalyst.

TPD of adsorbed pyridine shows that there is a decrease in the weak-medium acidity with the increase of pre-treatment temperature SZ > SZ250 > SZ350 = SZ500. Also the strong acidity decreases in the same order, but the ratio weak-medium/strong acidity shows a maximum for SZ250.

FT-IR spectra of adsorbed pyridine on the samples pre-treated thermally indicate the presence of Lewis and Brönsted acid sites. The ratio of B/L acid sites passes through a maximum between 100 and 250 °C, the same behavior is observed favoring the formation of bicyclic compounds.

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