

Hydration of α -pinene catalyzed by acid clays

Research Article

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Received 16 October 2012; Accepted 23 December 2012

Abstract: The hydration reaction of α -pinene in the presence of natural clays treated with monochloroacetic acid as catalyst to obtain oxygenated compounds was studied. Catalysts were characterized using X-ray diffraction, differential thermal analysis, programmed thermal desorption of adsorbed pyridine, and infrared spectroscopic analysis of adsorbed pyridine to determine Brønsted and Lewis acid sites. Catalytic tests revealed that treatment of the natural clay with the acid improved the catalytic activity and the selectivity toward oxygenated products by increasing the acidity of the catalyst. The selectivity toward oxygenated compounds increased with the augment of the α -pinene conversion because of greater contact between water molecules with the remaining α -pinene molecules. The natural clay without treatment produced compounds resulting from α -pinene isomerization, whereas the treated clays produced alcohols and other products in addition to isomerization compounds. After a certain time, the α -terpineol was isomerized into cineols. Studies of the reusability of the JAL catalyst were performed (clay treated with monochloroacetic acid). As the number of reuses increased, the percent conversion decreased; however, the selectivity toward oxygenated compounds increased.

Keywords: Monochloroacetic acid • Hydration • α -pinene • Cineols.

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1. Introduction

α -Pinene is a natural monoterpene with multiple uses, including applications in the food, fragrance and pharmaceutical industries [1] as well as in the preparation of chemical intermediates, such as the camphene used in the production of camphor.

The acid catalyzed hydration reaction is used to obtain oxygenated compounds, such as alcohols, aldehydes, and epoxides used in the perfume industry [2]. The hydration reaction of α -pinene produces a mixture of monocyclic and bicyclic alcohols, as well as monocyclic and bicyclic isomerization products because both reactions (hydration and isomerization) are catalysed by strong acids. A considerable number of investigations of the isomerization reaction of α -pinene using different catalysts have recently been reported [3-11].

Frequently, strong acid (sulfuric or phosphoric acid) catalysts are used in the industrial processing

of hydration products; however, the final disposal of reaction residues that contain these acids is harmful to the environment. For this reason, solid acid catalysts have been studied over the past few years with the aim of replacing traditional homogeneous processes with heterogeneous processes.

Among monocyclic alcohols, α -terpineol is the most important product used in the production of fragrances; α -terpineol also exhibits antimicrobial activity and is used for wound healing and the treatment of insect bites. 1,8-Cineol and 1,4-cineol are used in flavourings, fragrances, cosmetics and numerous brands of mouthwash; like α -terpineol, they too are used as an insecticide and insect repellents.

α -Terpineol can be obtained through the hydration of α -pinene; several studies have reported the hydration of α -pinene using homogeneous as well as heterogeneous catalysts. Roman-Aguirre *et al.* [12] used monochloroacetic acid or oxalic acid and obtained

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conversions of approximately 80% with α -terpineol selectivities of 70%; however, the disposal of the waste was difficult because the reaction was performed in a homogeneous medium. Robles *et al.* [13] used phosphotungstic acid as a catalyst in conjunction with a mixture of acetic acid and water to hydrate and acetylate α -pinene and limonene. These authors achieved 90% conversions with 85% selectivities toward alcohols as well as monocyclic and bicyclic acetates. They also supported the heteropolyacid on silica; however, under these conditions, the rate of conversion decreased, and a high percentage of isomerization products was obtained. Van der Waal *et al.* [14], Vital *et al.* [15,16] and Castanheiro *et al.* [17,18] used zeolites and phosphomolybdic acid on polymeric membranes to achieve total conversions with 50% and 75% selectivities, respectively, toward α -terpineol for 150 h of reaction at room temperature. Mochida *et al.* [19] reported the use of zeolites to obtain 100% conversion with 57% selectivity toward total alcohols. Yadav *et al.* [20] studied the acetylation and hydration of limonene and α -pinene using zeolites exchanged with metallic cations and rare earths; they obtained conversions up to 100% with selectivities toward oxygenated products that did not exceed 40%. Ávila *et al.* [21] used trichloroacetic acid on hydrated zirconium oxide to obtain 57% conversion with 75% selectivity toward total alcohols and 57% selectivity toward α -terpineol. Although the obtained results are interesting, the trichloroacetic acid is difficult to handle. Wijayati *et al.* [22] also used trichloroacetic acid on Y-zeolite and achieved 66% conversion and 58% selectivity toward α -terpineol. Recently, Kozevnikov *et al.* [23] modelled the chemical and phase equilibria of α -pinene hydration in subcritical CO_2 . Although the hydration reaction is continually under study, the best results obtained to this point involve the use different acids in liquid media, and few results have been reported for solid systems, where the problem of the catalyst leaching from the solid can occur because the reaction proceeds in the presence of water.

The performance of α -pinene hydration is limited by several problems: a) the reaction rate is slowed by the slow transference when it proceeds in a biphasic system; b) hydration reactions tend to be highly reversible; c) the competition between the isomerization reaction and the hydration reaction to achieve high selectivities toward oxygenated products at reasonable conversions depends strongly on the experimental conditions (*e.g.* the reaction time, the temperature, the solvent, the α -pinene/water/solvent ratio and the amount of catalyst). Consequently, further studies are required to achieve active, selective and stable catalysts that can be applied on an industrial scale.

In this study, relevant results of the hydration of α -pinene using bentonite clays treated with monochloroacetic acid are presented. The experimental conditions selected correspond to those that were found to be the most adequate in a previous study where trichloroacetic acid on hydrated zirconium oxide was used as a catalyst [21].

2. Experimental procedure

2.1. Catalysts

Natural bentonite clay (J) from San Juan province, Argentina, was used as a raw material for the preparation of the catalysts. The bentonite was treated with monochloroacetic acid (MCA) aqueous solution (1.3% wt/vol), and the clay/MCA ratio was maintained at 50% wt. The pH of the MCA aqueous solution prior to it contacting the clay was 2.0. After 24 hours of contact between the clay and acid solution, the pH increased to 2.2. The solid was subsequently separated by centrifugation. A portion of solid was dried at 60°C and named JA. The other portion was washed four times with distilled water until its pH was 5 and was subsequently also dried at 60°C; this sample was named JAL.

2.2. Catalytic tests

The catalytic tests were performed in a 200 cm³ three-necked glass reactor equipped with a refrigeration unit and a thermocouple. The reactor was submerged in a thermostatic bath filled with silicone oil and equipped with a magnetic stirrer. In batch experiments, 3.84 mmol of α -pinene, 10 mL of water and 6.8 mL of isopropyl alcohol were first added to the reactor. After the mixture was heated to 80°C, the catalyst was added. Aliquots were extracted with a micropipette at fixed times and were immediately analyzed with a Shimadzu GC17 gas chromatograph equipped with a FID and a capillary SPB5 Supelco column (30 m \times 0.25 mm \times 0.25 μm). The column temperature was increased from 60°C to 120°C at a heating rate of 2°C min⁻¹; it was then heated to 170°C at a heating rate of 10°C min⁻¹ and held at 170°C for 3 min.

Reaction products were identified by comparing the retention times of terpene standards or by using their Kovats index with confirmation by mass spectrometry.

2.3. Characterisation

Chemical analyses of the solid were obtained via inductively coupled plasma emission spectroscopy (ICP) using the fusion dissolution technique. The crystalline structures of the catalysts were studied using X-ray diffraction, which was performed on a Philips PW3710

Table 1. Chemical analysis of clay J.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	LOI*
J	53	15.9	1.3	1.2	5.3	2.6	0.8	0.2	16

*Loss by calcination

Table 2. Percent mass losses of catalysts at temperatures between 25°C and 500°C.

Catalyst	Mass loss
J	14.4
JA	18.8
JAL	18.6

X'PERT control unit equipped with a Cu K α radiation source ($\lambda = 1.5378 \text{ \AA}$, 40 kV, 20 mA) and a nickel filter. The MCA in the catalysts was analyzed via FT-IR using a Perkin-Elmer Spectrum RX and via thermogravimetric studies using a Shimadzu TA-60 WS. The acidity of the catalyst was investigated via the desorption of pyridine in a Shimadzu TA-60 WS thermogravimetric analyser. The nature of the acid centres (Brønsted and Lewis acidities) of the catalysts was studied through the adsorption of pyridine using FT-IR (Perkin-Elmer Spectrum RX1). Self-supported wafers (12 mg cm^{-2}) were prepared from the finely divided powders. These wafers were placed in a container saturated with pyridine for 24 h. The wafers were left in an air flow for 12 h to eliminate the physisorbed pyridine, and the spectrum was subsequently recorded at room temperature. Brønsted and Lewis sites were identified by the appearance of bands at $1535\text{--}1550 \text{ cm}^{-1}$ and $1440\text{--}1450 \text{ cm}^{-1}$, respectively. To analyse the adsorption of the reagents (α -pinene and water) on the catalysts, isothermal adsorption experiments were performed in a thermobalance, as previously described. The catalysts were placed in a container saturated with water or α -pinene for 24 h and were then desorbed by being heated to 500°C at a rate $10^\circ\text{C min}^{-1}$; the amounts of desorbed reagents were determined by the mass difference. The desorption of isopropyl alcohol, which was used as a solvent in the reaction, was also studied using this methodology to determine whether alcohol competes for catalyst sites that need reagents to react.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. Structural properties

A chemical analysis of natural bentonite (J) from San Juan Province, Argentina, is shown in Table 1 and corresponds to a typical composition of bentonite clay [24].

According to the X-ray diffraction results, the predominant phase in the natural bentonite was montmorillonite, and small amounts of quartz and feldspar were present as impurities [25]. Fig. 1 shows the $d(001)$ spacing of the montmorillonite measured by X-ray diffraction; this spacing represents the distance from the top of the Si tetrahedral silica sheet (T) to the top of the Si tetrahedral sheet of the adjacent layer of the clay mineral. The measurement therefore includes the T-O-T-type layer and the net interlayer spacing where the interlayer cations are situated. After the MCA treatment with and without washing (samples JAL and JA), the interlayer spacing slightly decreased from 14.99 \AA (sample J) to 14.66 \AA and 14.57 \AA for samples JAL and JA, respectively, and the peaks were broadened. The change in spacing values of the montmorillonite can be attributed to the replacement of the interlayer inorganic natural cations of the clay by the H^+ ions of the acid. Because the pH of natural bentonite (J) in an aqueous suspension is 6.2, the pH decreased 2.2 and 5 after treatments with MCA solutions without and with washing, respectively, as previously discussed.

To verify the possible influence of MCA in the solid acid, thermogravimetric studies were performed. Table 2 shows mass loss of catalysts J, JA and JAL after they were thermally treated at 500°C . The clays JA and JAL experienced similar mass loss, whereas the clay J weight loss is smaller. The weight loss of clays JAL and JA was 4.4% and 4.2% respectively, these values can be attributed to monochloroacetic acid residues that have been left on the catalyst surface.

The similarity in the mass losses of catalysts JA and JAL suggests that the first washing removes the MCA acid not retained and that subsequent washings have a negligible effect.

To confirm the hypothesis that only a small portion of MCA is retained on the acid-treated clays, FT-IR studies were performed on the solids. Fig. 2 shows the spectra of clay J, monochloroacetic acid (MCA) and clays JA and JAL. The FTIR spectrum of the original clay, J, contains bands characteristic of montmorillonite (3623 cm^{-1} (Al-Mg-OH stretching), 3438 cm^{-1} (H-O-H stretching), 1110 cm^{-1} (Si-O-Si stretching), 1025 cm^{-1} (Si-O-Si stretching), 914 cm^{-1} (Al₂OH bending), 837 cm^{-1} (Al-Mg-OH bending), 519 cm^{-1} (Si-O-Al bending) and 463 cm^{-1} (Si-O-Si bending)) [26], which is the main mineralogical component of bentonite. The band in the $3650\text{--}3600 \text{ cm}^{-1}$ region is

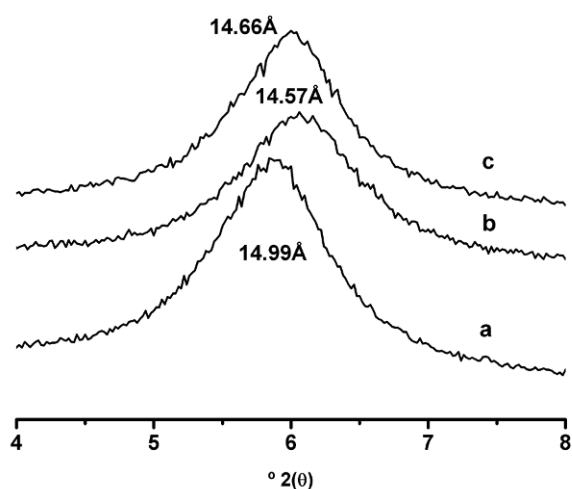


Figure 1. The d(001) spacing of the clay mineral catalysts. a: natural clay J, b: JA and c: JAL.

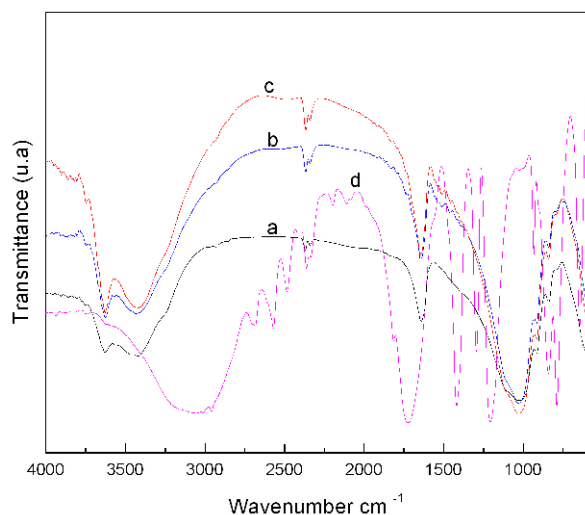


Figure 2. FTIR spectra of J, JA and JAL a: natural clay J, b: JA, c: JAL and d: MCA.

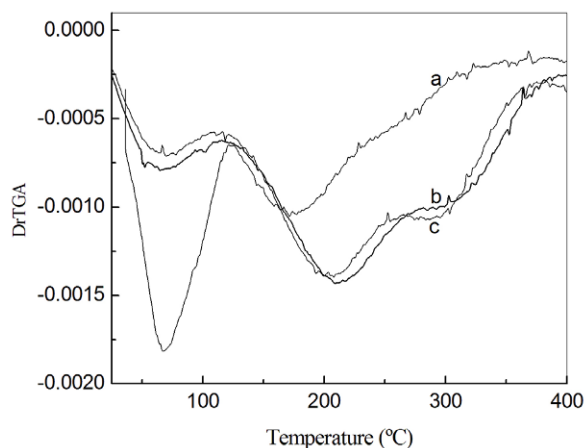


Figure 3. Desorption profiles of pyridine from the clays, which indicate the strength of the acid sites. a: natural clay J, b: JA and c: JAL.

assigned to the OH groups of the OH-Al/OH-Mg bonds in the clay. The bands at 3620 cm^{-1} in the spectra of clays JA and JAL became sharper after the clays were treated with MCA. This observation most likely indicates interaction of MCA with the OH-Al bonds. The band of H-O-H at 1640 cm^{-1} , similar to the band in the region of $1000\text{--}1100\text{ cm}^{-1}$, became sharper after the acid treatment. Bands assigned to MCA acid were not observed in the spectra of clays JA and JAL, which coincides with the weight-loss results. Therefore, the acid appears to interact only with the interlayer cations such that the structure of the clay remains intact.

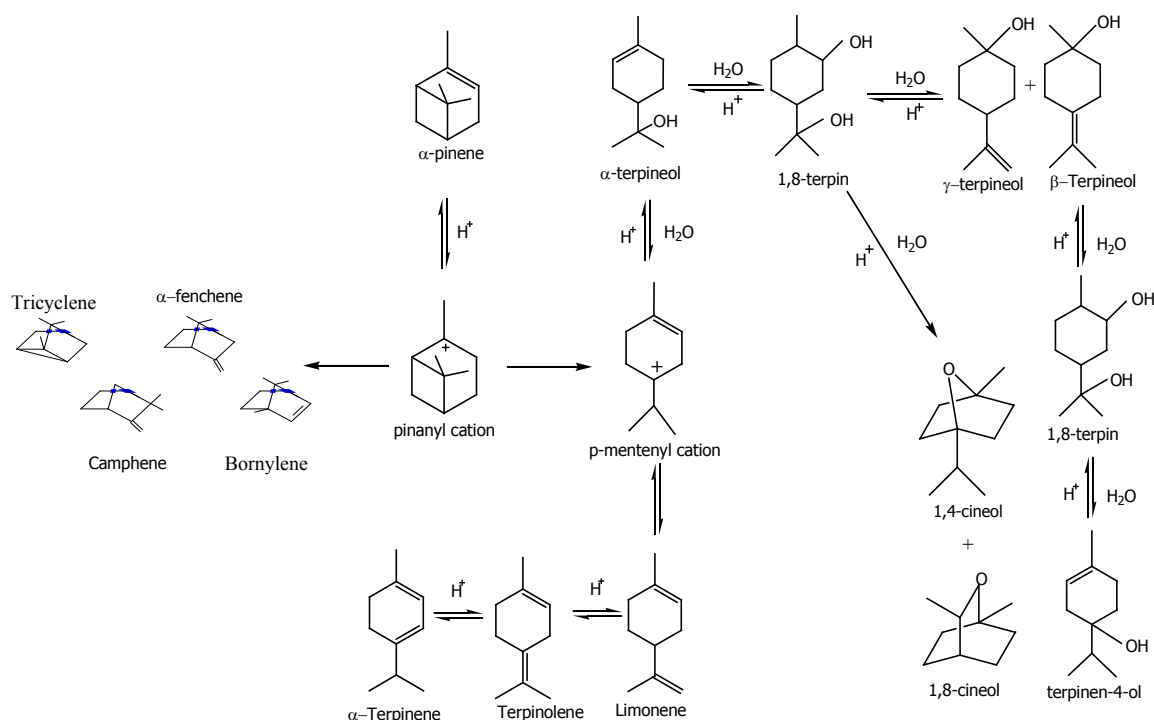
3.1.2. Acid properties

The desorption of adsorbed pyridine was measured using thermogravimetry to determine the strength of the acid sites. The interaction between a site and a pyridine molecule determine the strength of the acid site: greater pyridine desorption temperatures indicate greater site strength. Fig. 3 shows the derivative of the TGA trace as a function of the temperature; the derivative curve shows that the minima shift toward higher temperatures for catalysts JA and JAL, which exhibit correspondingly greater acidities. Thus, the derivative of the TGA trace for natural clay J contains two minima: one at 70°C , which corresponds to water desorption, and the other at 170°C . In contrast, the derivatives of the TGA traces of JA and JAL exhibit three minima: the temperature at which the first minimum occurs coincides with the minimum observed for sample J, whereas the second occurs at 170°C for J and at 213 and 202°C for JA and JAL, respectively. Finally, the third minimum at 297°C only appears in the TGA trace of the clays treated with MCA.

The presence of Brønsted and Lewis acid sites was studied via the adsorption of pyridine, which was monitored using FT-IR. Fig. 4 shows the FT-IR spectra of J, JA and JAL with adsorbed pyridine. Clay J exhibits weak Brønsted acidity. When the clay was treated with MCA, its acid properties were modified. The spectra of samples JA and JAL exhibited only one band, at approximately 1540 cm^{-1} , which was due to the existence of Brønsted acid sites and was the most intense band in the spectrum of clay JA; in contrast, the spectrum of JA contained no bands associated with Lewis acid sites.

3.2. Hydration reaction of α -pinene

α -Pinene, in the presence of an acid catalyst, is attacked by a proton to form a carbocation [27]. This carbocation undergoes a rearrangement that either maintains the bicyclic structure of α -pinene or induces ring-opening of its four-carbon ring to generate other carbocations. All of these carbocations can lose a proton and generate



Scheme 1. Scheme of the hydration reaction of α -pinene.

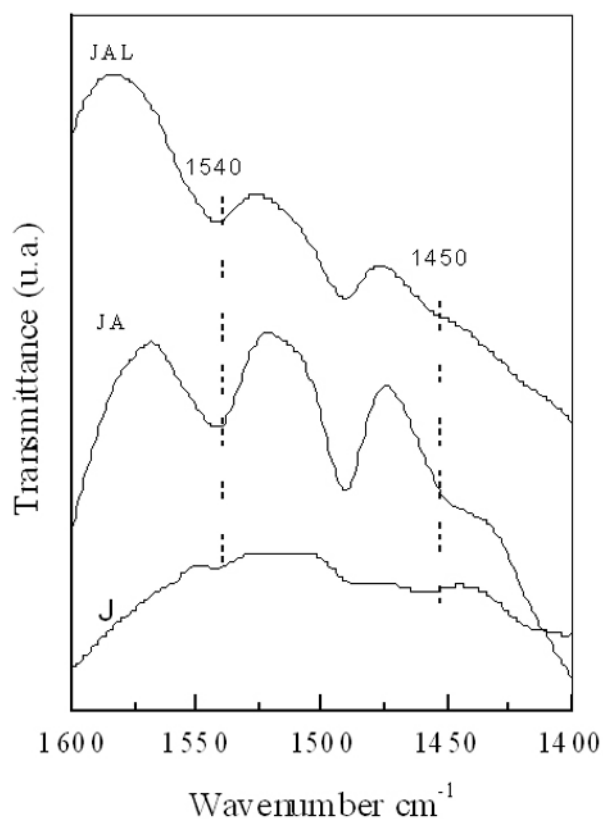


Figure 4. FTIR spectra of catalysts with adsorbed pyridine a: natural clay J, b: JA and c: JAL.

monocyclic and bicyclic hydrocarbons or, in the presence of a nucleophile, result in the formation of monocyclic and bicyclic alcohols (see Scheme 1).

The kinetic behaviour of the hydration reaction of α -pinene was studied using 0.6 mL of α -pinene, 10 mL of H_2O , 6.8 mL of $(\text{CH}_3)_2\text{CHOH}$, 200 mg of catalyst JAL and a temperature of 80°C . The results are shown in Fig. 5. This figure shows the concentration of α -pinene, the reaction products found in the greatest proportion and the products found in concentrations less than 5%, which are grouped as hydrocarbons and oxygenated compounds. The oxygenates found in concentrations less than 5% were fenchone, fenchol and borneol; the hydrocarbons found in concentrations less than 5% were camphene, carene, γ -terpinene and terpinolene.

The rate of α -pinene consumption was pronounced for reaction times up to 400 minutes; after 400 minutes, the consumption rate was slower. Reaction products began to be produced from the beginning of the reaction; they were formed by reactions in parallel. The limonene and the sum of hydrocarbons with concentration less than 5% increased slightly with increasing reaction time. Among oxygenated compounds, the α -terpineol was produced in the greatest proportion; its concentration increased for reaction times up to 400 min and then began to decrease, which is similar to the behaviour observed by Wijayati *et al.* [22].

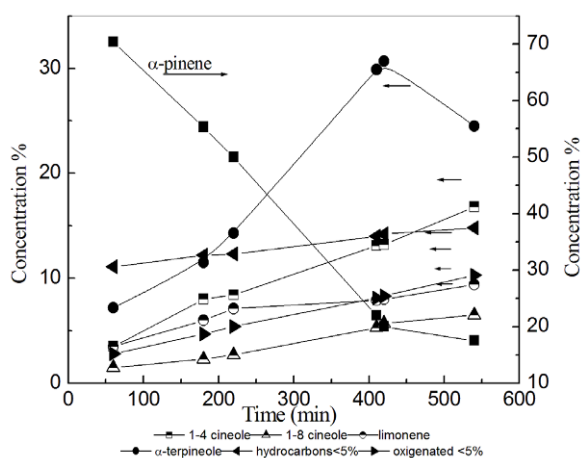


Figure 5. Hydration of α -pinene on JAL. Concentration vs. time. Reaction conditions: 0.6 mL of α -pinene, 10 mL of H_2O , 6.8 mL of $(\text{CH}_3)_2\text{CHOH}$, 200 mg of catalyst and a temperature of 80°C .

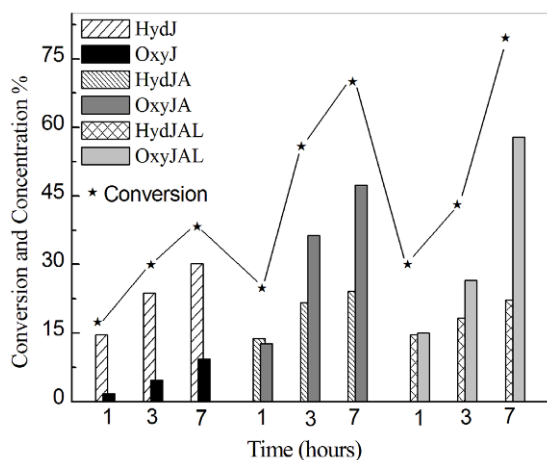


Figure 6. Reaction products: hydrocarbons and oxygenated. Conversion for α -pinene hydration.

The α -terpineol in an acid medium can be isomerized, and when the α -pinene concentration is small, other reactions are expected to predominate; thus, the reaction time must be a controlled variable when α -terpineol is the synthesis target. The sum of the concentrations of oxygenated compounds with concentrations less than 5% increases continuously.

Cineols are obtained from rearrangements of terpenyl hydrate and α -terpineol [28,29]. Recently, Guyeskava *et al.* [30] obtained 1,4-cineol and 1,8-cineol from α -terpineol using phosphotungstic acid as a catalyst.

The kinetic behaviours of catalysts J, JA and JAL during three reaction times (*i.e.*, 1, 3 and 7 h) were studied using 0.6 mL of α -pinene, 10 mL of H_2O , 6.8 mL of $(\text{CH}_3)_2\text{CHOH}$ and 200 mg of catalyst; the results are shown in Fig. 6. The concentration of reaction products for the three catalysts increased with increased reaction time. A different behaviour was observed between

the untreated clay (J) and the clays treated with monochloroacetic acid (JA and JAL). The untreated clay produced mostly reaction products of α -pinene isomerization. With the treated clays, the concentration of the isomerization products was the same as that of the oxygenated compounds at the beginning of the reaction (1 h); however, with longer reaction times, oxygenated compounds became the major products.

Clay J resulted in the lowest conversion of α -pinene, and this result is in agreement with the low acid strength of this clay observed in the acidity studies. Most of the conversion observed at short reaction times for clay JA relative to that of JAL can be attributed to the greater acid strength of JA, as determined by the pyridine temperature-programmed desorption and by the increased intensity of the band associated with Brønsted acid sites in the FTIR spectrum of JA.

The adsorption of the reagents water and α -pinene was studied by measuring the amounts of reagent desorbed from the catalyst surface under the assumption that the amount of reagent desorbed is directly related to the amount of reagent adsorbed. Table 3 shows the desorption of α -pinene and water on clays J, JA and JAL at temperatures from 30°C to 500°C . The ratio between the amount of adsorbed water and the amount of adsorbed α -pinene is less than 1 in the case of the untreated clay. For the clays treated with monochloroacetic acid, the situation is reversed, and the ratios are 2.5 and 4.1, respectively. Clay J produces mainly isomerization products because the catalyst surface is almost completely covered with α -pinene, and water molecules necessary for the hydration reaction cannot access the acid sites; consequently, the α -pinene molecules undergo rearrangements and are transformed into the corresponding isomers.

Isopropyl alcohol is used as a solvent to obtain a homogenous reaction system. The solvent may compete with reagents for acid sites, so the adsorption of isopropyl alcohol was also studied. The alcohol is assumed to compete with water for adsorption onto sites because both are polar; nevertheless, the adsorption of isopropyl alcohol onto the untreated clay was negligible, as was the amount adsorbed onto the treated clays. We therefore concluded that no competition exists between isopropyl alcohol and the reagents for the acid sites.

The selectivity toward oxygenated compounds as a function of the conversion percentage is shown in Fig. 7. The untreated clay (J) exhibited a low selectivity, whereas clays treated with MCA exhibited higher selectivities. The selectivity behaviours of JA and JAL were practically the same. All of the catalysts showed increased selectivity toward oxygenated compounds as the reaction proceeded. When the α -pinene is

consumed, the probability of water molecules reaching the acid sites and reacting with the remaining α -pinene to produce hydration reactions increases. In agreement with these results, we observed greater selectivity toward oxygenated compounds for the catalyst JAL, which exhibited a greater ratio water/ α -pinene ratio (see Table 3).

If the mass ratio is taken into account, then the terpene/catalyst ratio required to achieve a reasonable rate of reaction for the hydration reaction oscillates between 4/1 and 1.5/1. The price of a catalyst becomes an important variable in the time-of-cost analysis. In a previous work [21], a catalyst prepared from zirconium hydroxide impregnated with trichloroacetic acid (TCA) was used. FTIR and XPS studies confirmed the presence of TCA in the catalyst. Promising results (*i.e.*, conversions of approximately 75% and selectivities toward oxygenated compounds of approximately 75%) were obtained. Because TCA is corrosive, we proposed

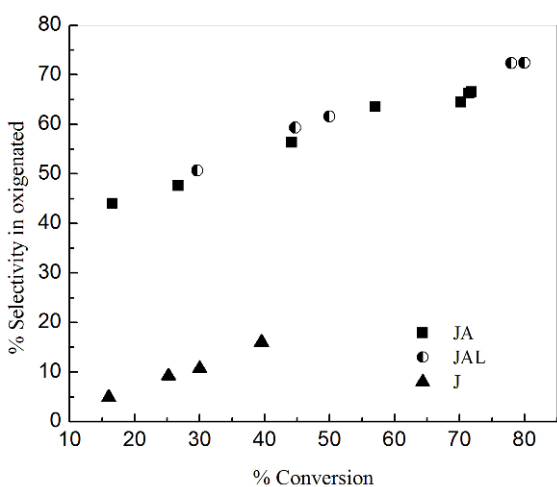


Figure 7. Selectivity toward oxygenated products vs. the percent conversion for different catalysts.

Table 3. Adsorption of α -pinene and water at temperatures between 30°C and 50°C, expressed as percentages.

	(%) Water	(%) α -pinene	Ratio water/ α -pinene adsorbed
J	0.1	0.3	0.3
JA	23.8	9.4	2.5
JAL	21.5	5.3	4.0

Table 4. Hydration of α -pinene after different runs with catalyst JAL.

Time (min)	X (%) first run	X (%) second run	X (%) third run	S (%) alcohols first run	S (%) alcohols second run	S (%) alcohols third run
200	52	35	30	58	70	80
400	77	53	49	72	83	85

Reaction conditions: 0.6 mL of α -pinene, 10 mL of H_2O , 6.8 mL of $(CH_3)_2CHOH$, a temperature of 80°C and 200 mg of catalys

the use of MCA and the use of a less expensive support than zirconium hydroxide to enable the application of the catalyst to an industrial process; we consequently chose a clay support for the present study.

The purpose of the present work was to support the MCA on a low-cost solid to prepare a heterogeneous catalyst. The impregnation method of natural clay in a solution of 50% MCA was used for this purpose; however, FTIR studies of the catalyst showed a lack of carbonyl signals characteristic of an organic acid. These results allow us to conclude that the principal function of the acid was to exchange cations in the clay with protons, which resulted in an acidic clay. The results attained in this study (*i.e.*, 80% of conversion X and 70% of selectivity (S) in oxygenated compounds) are lower than those reported by Aguirre *et al.* [13] with respect to the selectivity toward α -terpineol; however, among the oxygenated products, a mixture of 1,4- and 1,8-cineol was obtained, which are high-value products. However, the separation of a solid catalyst from a reaction medium is easier than the method by cooling proposed for the separation of the homogeneous catalyst, which implies an additional energetic cost.

The mass of catalyst necessary to process 1 kg of α -pinene using JA (0.39) is slightly less than that required in the homogeneous process (0.58). Notably, the handling of large amounts of MCA requires safety precautions to avoid exposure to the acid, whereas clays are practically harmless.

3.3. Reusability of JAL

Given that the clay treated with monochloroacetic acid (MCA) exhibits satisfactory results for its use on an industrial scale (see Figs. 6 and 7), three consecutive catalytic runs were performed to study the deactivation of the catalyst JAL. After the first run, the catalyst was separated from the reaction mixture and used in a second and third run with new reagents. Table 4 shows the observed conversion and selectivity values after different reaction times and different runs. The catalytic activity decreased in the second and the third runs for both reaction times, whereas the selectivity toward alcohols increased, albeit more slowly after the third run. This behaviour is similar to that observed by Avila *et al.* [21], who used trichloroacetic acid on hydrated

zirconium oxide. The FTIR spectrum of the used sample of JAL indicated that the acid sites were not modified. Brønsted sites with the same acidities were observed in the fresh catalyst and in the used JAL catalyst.

4. Conclusions

Natural bentonite clay treated with monochloroacetic acid (MCA) is a useful catalyst for the hydration reaction of α -pinene. Conversions of approximately 80% with selectivities toward oxygenated compounds of 70% were observed, where α -terpineol was the major component. The acid treatment increased the acid strength of the natural clay and resulted in Brønsted acid centres. This increased acidity is responsible for the greater activities of the treated acid clays relative to that of the untreated clay. After the acid treatment, only a small amount of MCA remains in the clay.

The selectivity of oxygenated products increased with the degree of conversion because of the greater

availability of water molecules to the acid sites. When used as a catalyst, the natural clay resulted mainly in isomerization compounds.

After three consecutive uses, the catalyst exhibited a lower activity but a greater selectivity toward oxygenated compounds, and the FT-IR signals that correspond to the Brønsted acid sites were maintained.

A comparison of the catalyst studied here with other catalysts that operate in the homogeneous or heterogeneous phase reveals that the natural clay treated with MCA exhibits a reasonable activity toward the production of α -terpineol and cineols. The catalyst investigated here is an economical catalyst that is easily handled because it is a solid with low toxicity.

Acknowledgements

We thank CONICET, ANPCyT and UNSL for financial support to perform this work and Dr. Esther Ponzi for her contributions to the discussion of the results.

References

- [1] S. Findik, G. Gündüz, *J. Am. Oil Chem. Soc.* 74, 1145 (1997)
- [2] W. Erman, *Chemistry of the Monoterpenes* (Marcel Dekker, New York, 1985)
- [3] A. Severino, A. Esculcas, J. Rocha, J. Vital, L. Lobo, *Appl. Catal. A-Gen.* 142, 255 (1996)
- [4] C. Lopez, F.C. Machado, K. Rodriguez, B. Mendez, M. Hasegawa, S. Pekerar, *Appl. Catal. A-Gen.* 173, 75 (1998)
- [5] E. Unveren, G. Gündüz, F. Cakicioglu-Özkan, *Chem. Eng. Commun.* 192, 386 (2005)
- [6] G. Gündüz, R. Dimitrov, S. Yilmaz, L. Dimitrov, M. Spassova, *J. Mol. Catal. A-Chem.* 225, 253 (2005)
- [7] N. Comelli, E. Ponzi, M. Ponzi, *Chem. Eng. J.* 117(2), 93 (2006)
- [8] R. Rachwalik, Z. Olejniczak, J. Jiao, J. Huang, M. Hunger, B. Sulikowski, *J. Catal.* 252, 161 (2007)
- [9] L. Mokrzycki, B. Sulikowski, Z. Olejniczak, *Catal. Lett.* 127, 296 (2009)
- [10] J. Wang, W. Hua, Y. Yue, Z. Gao, *Bioresour. Technol.* 101, 7224 (2010)
- [11] B. Atalay, G. Gündüz, *Chem. Eng. J.* 168, 1311 (2011)
- [12] M. Román-Aguirre, L. De la Torre-Sáenz, W. Antúnez Flores, A. Robau-Sanchez, A. Aguilar Elguezabal, *Catal. Today* 107, 310 (2005)
- [13] P. Robles-Dutenhefner, Kelly da Silva, M. Rafiq, H. Siddiqui, I. Kozhevnikov, E. Gusevskaya, *J. Mol. Catal. A-Chem.* 175(1-2), 33 (2001)
- [14] J. van der Waal, H. van Bekkum, J. Vital, *J. Mol. Catal. A-Chem.* 105, 185 (1996)
- [15] J. Vital, A.M. Ramos, I.F. Silva, H. Valente, J.E. Castanheiro, *Catal. Today* 56, 167 (2000)
- [16] J. Vital, A.M. Ramos, I.F. Silva, J.E. Castanheiro, *Catal. Today* 67, 217 (2001)
- [17] J. Castanheiro, A. Ramos, I. Fonseca, J. Vital, *Catal. Today* 82, 187 (2003)
- [18] J. Castanheiro, I. Fonseca, A. Ramos, R. Oliveira, J. Vital, *Catal. Today* 104, 296 (2005)
- [19] T. Mochida, R. Ohnishi, N. Horita, Y. Kamiya, T. Okuhara, *Micropor. Mesopor. Mat.* 101, 176 (2007)
- [20] M. Yadav, M. Patil, R. Jasra, *J. Mol. Catal. A-Chem.* 297, 101 (2009)
- [21] M. Ávila, N. Comelli, E. Rodríguez-Castellón, A. Jiménez-López, R. Carrizo Flores, E. Ponzi, M. Ponzi, *J. Mol. Catal. A-Chem.* 322, 106 (2010)
- [22] N. Wijayati, H. Dwi Pranowo, Jumina, Triyono, *Indo. J. Chem.* 11(3), 234 (2011)
- [23] A. Chibiryaev, A. Yermakova, I. Kozhevnikov, *J. Supercrit. Fluid* 51, 295 (2010)
- [24] R.E. Grim and N. Güven, *Bentonite-Geology, Mineralogy, Properties and Uses* (Elsevier, Amsterdam, 1978) 256
- [25] C. Volzone, J. Rinaldi, J. Ortiga, *J. Environ. Manage* 79, 247 (2006)

- [26] V. Farmer (Ed.), *The Infrared Spectra of Minerals*. Monograph 4 (Mineralogical Society, London, 1974)
- [27] G.A. Olah, G.K. Surya Prakash, A. Molnár, J. Sommer, *Superacid Chemistry*, 2nd edition (Wiley & Sons, USA, 2009) 707
- [28] Patent US 1,994,131 (1935)
- [29] Patent US 4,831,163 (1989)
- [30] E. Leão Lana, K. da Silva Rocha, I. Kozhevnikov, E. Gusevskaya, *J. Mol. Catal. A-Chem.* 259, 99 (2006)