SYNTHESIS OF TERPINEOL FROM α-PINENE CATALYZED BY TCA/Y-ZEOLITE

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ABSTRACT

The hydration of α-pinene has been studied in the presence of TCA/Y-Zeolite catalyse. The catalyst was prepared by impregnating trichloroacetic acid (TCA) on support of Y-Zeolite. The TCA/Y-Zeolite catalyst converted α-pinene into hydrocarbons, while the TCA/Y-Zeolite catalyst was active and selective for producing alcohols, with a conversion of 66% and showed 55% selectivity for α-terpineol at 10 min. The reaction taken place in a solid–liquid mode and most of the α-terpineol is extracted out by the organic phase during the course of the reaction. TCA/Y-Zeolite was found as good catalyst for hydration of α-pinene to produce α-terpineol.

Keywords: *α–pinene; TCA/Y-Zeolite; terpineol*

INTRODUCTION

The acid hydration of α-pinene yielded a complex mixture of monoterpenes, alcohols and hydrocarbons [1-4]. The resulting terpenic alcohols are valuable products with many applications in the pharmaceutical industry. From commercial viewpoints, α-terpineol, 4-terpineol, and terpineol hydrate are the most interesting derivatives of α-pinene. Alpha-Terpineol exhibited antimicrobial activity and was used for wound healing and insect bites [5-8].

Upon subjecting α-pinene to aqueous mineral acids, complex mixtures was obtained from isomerization and hydration [9-10] The main product (Fig. 1.) was the monocyclic alcohol of α-terpineol and the minor products were camphene, limonene as well as terpinolene.

The synthesis of alcohols from α-pinene in the presence of different catalysts had been well and intensively studied in the last ten years. Vital et al. [1] 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 selectivity for α-terpineol around 50% to 70%, although it required 150 h of reaction time. Patricia et al. [12] used phosphotungstic acid ($HPW_{12}O_{40}$) as a catalyst and mixture 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

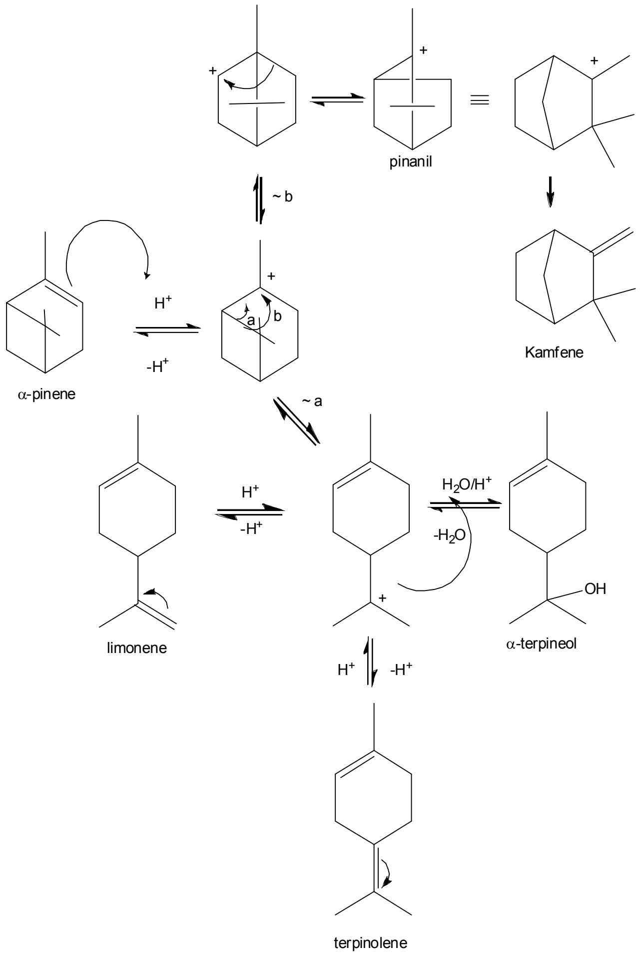

Fig 1. Hydration reaction scheme of α-pinene

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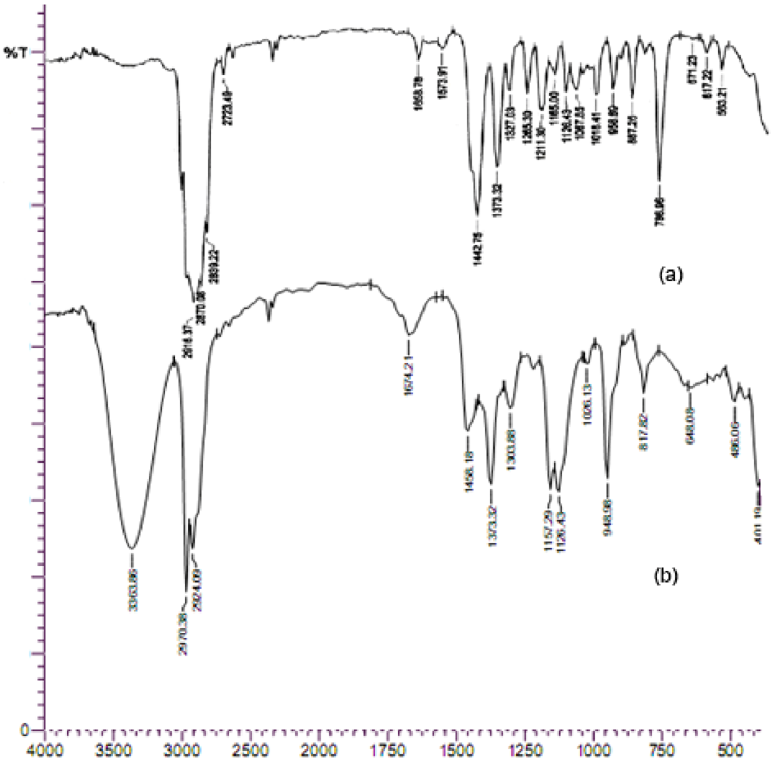

Fig 2. FTIR spectra of a) α-pinene and b) α-terpineol as product hydration reaction of α-pinene with TCA/Y-Zeolite

reaction, with selectivity 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. [10], used oxalic or chloroacetic acid for the transformation of α-pinene and obtained conversion of 80% with selectivity of 70% for α-terpineol after 4 h, but the dissolved acid had to be separated. Mochida et al. [4] reported the use of zeolites catalyst for hydration reaction and obtained 100% conversion, but with low selectivity for alcohols (around 57%). Avila et al. [11] used the catalysts 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 nH_2O catalyst was active and selective for producing alcohols, with conversion of 57% and selectivity of 75% of total alcohols, and showed selectivity of 57% for α-terpineol.

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 [13-14]. In this study, relevant results of the hydration of α-pinene using trichloroacetic acid (TCA) supported on Y-zeolite (TCA/Y-Zeolite catalysts) was presented.

EXPERIMENTAL SECTION

Materials

α-Pinene was obtained from Sigma Aldrich, Germany. The zeolite used in this work, was obtained from Sigma Aldrich Chemical Company, Australia. The Y-zeolite was supplied in the ammonium form and was activated by heating at 823 K for 5 h in a furnace.

TCA/Y-Zeolite catalyst was prepared by impregnation of the corresponding support with the necessary amount of aqueous solution of TCA to obtain nominal loadings of 35%. The precursor was prepared by placing the mixture in erlenmeyer at 37 °C under stirring condition (100 rpm). The TCA/Y-Zeolite catalyst was obtained after drying the precursor at 110 °C for 10 h.

Instrumentation

Analysis of the reaction products was performed by Gas Chromatography (GC) (Hewlett Pacard 5890 Series II equipped with flame ionization detector/FID).

Table 1. Hydration of α-pinene over the TCA/Y-Zeolite catalyst[a]

	Time (min)					
	0	10	20	60	120	240
α-Pinene	100	33.6	25.2	20.9	6.6	0.4
Camphene	0	3.6	3.2	4.5	4.8	3.8
Limonene	0	7.1	7.1	10	12.2	15
Terpinolene	0	12.5	12.9	17.1	20.8	24.9
α-Terpineol	0	36.5	42.7	40.8	39.5	30.7

[a]Concentration profiles (%)

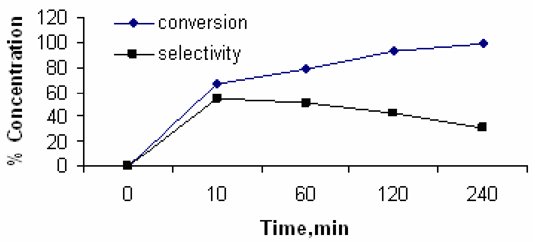

Fig 3. Conversion and selectivity of hydration of α-pinene to α-terpineol in the presence of TCA/Y-Zeolite catalyst vs time

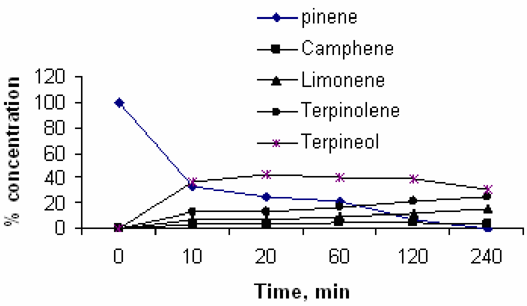

Fig 4 Concentration of reagent and products over TCA/Y-Zeolite catalyst vs. time

The column used was HP5 (% Phenyl Methyl Siloxane). The temperature of the column was adjusted to be 70 °C for 5 min and then increased to 280 °C by 10 °C/min. The carrier gas used was helium (He) (0.1µL/min flow). The injection and detection temperatures were set to be 280 and 300 °C, respectively and the split mode was 1/100. The various components were characterized by FTIR and GC-MS instrument.

Procedure

The catalytic tests were performed in a 100-cm^3 three-necked-glass reactor with condenser and thermocouple. The reactor was submerged in thermostatic bath with silicone oil and magnetic stirring. In batch experiment, 1.84 mmol of α-pinene, 2.5 mL of water and 3.4 mL of isopropyl alcohol were first placed. After heating to the desired temperature (65 °C), 400 mg of the catalyst was added. Aliquots were extracted with a micropipette and immediately analyzed with GC.

RESULT AND DISCUSSION

Analysis α-pinene and product with FTIR

The presence of -OH in the product was studied by FTIR. Fig. 2 showed the spectra of pure α-pinene and the product of hydration reaction of α-pinene with TCA/Y-Zeolite catalyst. The spectrum of α-terpineol as the hydration product exhibited diagnostic bands. Band at 3363 cm^{-1} was observed to stretching of the hydroxyl group of terpineol. The band at 1674 cm^{-1} and 1373 cm^{-1} were assigned to C = C bond of the alkene system and -CH3 group. Finally, the bands came from stretching and bending of C–O bond (C-O at the tertiary alcohol) was observed at 1157 and 1126 cm^{-1}.

Hydration reaction of α-pinene

Catalytic study was performed using TCA/Y-Zeolite. α-Pinene reacted with water in a molar ratio of 13:1 to afford monoalcohols. The reaction was carried out in an excess of water with α-pinene as the limiting reagent. α-Pinene was almost immiscible in water at the reaction conditions. It forms a separated organic phase in the reactor. The reaction taken place over the catalyst surrounded by the aqueous phase. The reaction product, i.e. α-terpineol, was non polar compounds and was extracted out into the organic phase simultaneously during of the reaction thereby giving significant conversion. Fig. 3 showed the conversion and selectivity results for TCA/Y-Zeolite catalyst.

α-Pinene was adsorbed on TCA/Y-Zeolite. After 10 min of reaction with TCA/Y-Zeolite, conversion of 66% and selectivity of 55% for α-terpineol were observed. Fig. 4 showed the reagent and products profiles obtained from the hydration of α-pinene catalyzed by TCA/HY-Zeolite. α-Pinene should be adsorb on the acid site to promote the acid catalyzed reaction in the presence of water.

α-Pinene in the presence of acid catalyst was attacked by proton to form carbocation. This carbocation might undergo rearrangement or ring opening of its four-carbon ring to produce other carbocations. All carbocations could lose a proton and generate monocyclic and bicyclic hydrocarbons or, in the presence of nucleophile, gave monocyclic alcohol (Fig. 1).

The hydration of α-pinene catalyzed by TCA/Y-zeolite was fast and produced monocyclic terpenes and alcohols with α-terpineol as a main product (Table 1). Actually, the typical way to obtain terpineol is by hydration of α-pinene with aqueous sulfuric acid [14]. However the separation of catalyst from the reaction products was too difficult and an environmental problem. According to this work, TCA/Y-Zeolite was good candidate for the industrial hydration of α-pinene, due to its easy separation from reaction products and low cost.

CONCLUSION

The TCA/Y-Zeolite catalyst converted α-pinene into hydrocarbons, while the TCA/Y-Zeolite catalyst was active and selective for producing alcohols, with a conversion of 66% and showed 55% selectivity for α-terpineol at 10 min. The good results were due to its strong acidity during reaction and its easy separation from reaction products. The yield obtained by using this catalyst was interesting for industrial application.

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REFERENCES

1. Vital, J., Ramos, A.M., Silva, I.F., Valente, H., and Castanheiro, J.E., 2000, *Catal. Today*, 56, 167–172.
2. Vital, J., Ramos, A.M., Silva, I.F., Valente, H., and Castanheiro, J.E., 2001, *Catal. Today*, 67, 217–223
3. Castanheiro J.E., Foseseca, I.M., Ramos, A.M., Oliveira, R., and Vital, J., 2005, *Catal. Today*, 104, 296–304.
4. Mochida T., Ryuichiro O., Naoto H., Yuichi K., Toshio O., 2007, *Microporous Mesoporous Mater.*, 101, 176–183.
5. Bhatia, S.P., 2008, *Food Chem. Toxicol.*, 46, 5275–5279.
6. Martino, L.D., Vinzenco, D.F., Carmen, F., Enrico, M., and Felice, S., 2009, *Molecules*, 14, 2735–2746.
7. Moreira, M.R., Cruz, G.M.P., Lopes, M.S., Albuquerque, A.A.C., and Cardoso, J.H.L., 2001, *J. Med. Biol. Res.*, 34, 1337–1340.
8. Bagheri, S.M, Amirhossein, S., Ahmad, R.G., Soodabeth, S., Maryam, M., and Mehrdad, I., 2010, *Pharm. Biol.*, 48, 3, 242–2463.
9. van der Waal, J.C., Van Bekkum, H., and Vital, J.M., 1996, *J. Mol. Catal. A: Chem.*, 105, 185–192.
10. Roman-Aguirre, M.R., De la Torre-Sáenz, L., Flores, W.A., Robau-Sánchez, A., and Elguézabal, A., 2005, *Catal. Today,* 107-108, 310–314.
11. Avila, M.C., Nora, A.C., Castellon, E.R., and Lopez A.J., 2010, *J. Mol. Catal. A: Chem.,* 322, 1-2 106–112
12. Robles-Dutenhefner, P.A., da Silva, K.A., Siddiqui, M.R.H., Kozhevnikov, I., and Gusevskaya, E.V., 2001, *J. Mol. Catal. A: Chem.*, 175, 33-42.
13. Zhang, H., Mahajani, S.M., Sharma, M.M., and Sridhar, T., 2002, *Chem. Eng. Sci.,* 57, 315-322.
14. Pakdel, H., Sharron, S., and Roy, C., 2001, *J. Agric. Food. Chem.,* 49, 9, 4337–4341.