

Isomerization of α -pinene in the terpenin oil with TCA/ Natural Zeolite using microwave irradiation

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Abstract: The catalytic potential of trichloroacetic acid (TCA)/Natural Zeolite in the isomerization of α -pinene in the terpenin oil was investigated. The purpose of this study is to investigate the influence of the power of microwave on activity and selectivity of catalyst. The main product were champhene, terpinene, limonene, p-cymene, and terpinolene. The highest selectivity was 28.26% with a conversion of 23.25%, whereas the higher conversion was 98.99% with selectivity of 16.90% at room temperature using power of microwave 640 W.

Keywords: α -pinene, isomerization reaction, microwave

1 Introduction

Turpentine oil are mobile liquids, usually non-colored or slightly colored, with characteristic pleasant odor. The boiling point of the oils varies between 154-170°C, and not soluble in water, but are soluble in ethers, dichloromethane and in other oils. Chemically, turpentine oil is mixture of cyclic monoterpene hydrocarbons, C₁₀H₁₆, such as α -pinene, β -pinene, 3-carene and d-longifolene. Alpha-pinene compound is a major component of turpentine oil (>80%). Synthesis of some compounds based α -pinene produce terpeneol, camphor, bornyl chloride, and camphene an industrial scale has a high selling price. Alpha-pinene can be converted chemically into the basic material for the manufacture of compound that is more useful through addition reaction, hydration reaction, and isomerization [1-4].

The isomerization α -pinene can produce bicyclic compound, monocyclic compound, or other products. Bicyclic product such as camphene, while products monocyclic such as limonene, p-cimene, and terpinolene [5]. The result isomerized α -pinene are used as fragrance ingredients, cosmetics, food, pharmaceuticals, flavorings, and solvent [6-7].

In chemical reactions, homogeneous catalysts can't be reused because it is unstable, besides the catalyst separation process of its products are widely experienced problems because both are in one phase. The homogeneous catalysts lead to the decomposition of the reaction products because of the homogeneous catalysts participate in the reaction. Heterogeneous catalysts can be used as an alternative with positive opportunities related to increased yields and selectivity through the isomerization reaction of α -pinene [8].

The chemical reactions using microwave is already done. Method of heating by microwaves has many advantages, such faster reaction time, the product is cleaner, higher selectivity and better results. This is



the main alternative to obtain a synthesis of various organic of intermediates the isomerization of compounds more efficiently, with operational simplicity and mild reaction conditions [9].

In this study the effect of power microwave to isomerization of α -pinene in The turpentin oil using TCA/ Natural Zeolite as heterogeneous catalystr

2 Experimental

2.1 Catalyst Preparation

Natural zeolites are dried and then activated. Natural zeolite has been activated, calcined at temperatures of 500 °C for 4 h in a calcining furnace. Furthermore, natural zeolites was impregnated with trichloroacetic acid at a concentration of 35% followed calcination at a temperature of 500 °C for 4 h. The catalyst was analyzed by X-Ray Diffraction (XRD) and acidity test by gravimetric method.

2.2 Catalytic test

The isomerization reaction α -pinene using turpentine oil as a raw material (α -pinene (87%), β -pinene (2%), and 3-carene (11%). The isomerization α -pinene in the turpentine oil 10 mL was performed in the flask by adding 1 g TCA/Natural zeolite catalyst. The mixture was reacted by using microwave at 320, 480, 640 and 800 W power for 15, 30, 45, 60 and 90 min. The mixture is separated by centrifugation for 15 min to separate catalyst and results, the reaction product is then filtered and analyzed by FTIR and GC-MS.

3 Result and Discussion

Trichloroacetic acid/natural zeolite is found as a good catalyst for the production of camphene from α -pinene. Impregnation is done by adding TCA to natural zeolite. The purpose of this process is that the active side of the TCA will be bound to the pore structure of zeolite solids. The good results are due to strong acidity and high affinity with organic and aqueous phases during reaction. The crystallinity structure of the catalyst was studied by XRD. The powder diffractograms of natural zeolite (ZA), and H-Natural Zeolite H-(ZA) showed reflection lines at 17°, 20°, 22°, and 25°, which were assigned to TCA (JPDC 42.1605), while in this case of TCA/ZA, the diffractogram did not show reflection lines corresponding to TCA. This was attributed to TCA dispersion due to the high surface area of the natural zeolite as the support [1]. (Figure 1).

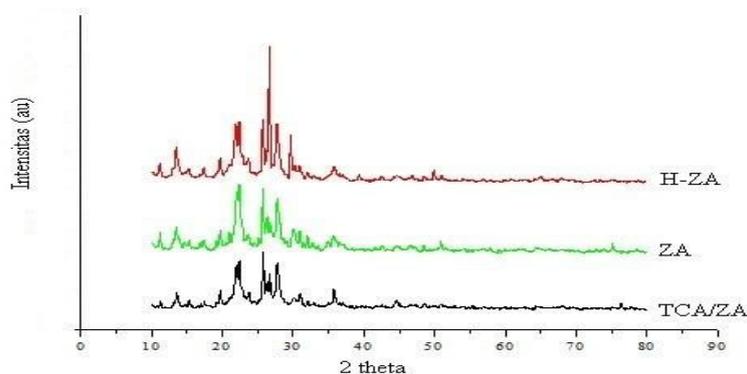


Figure 1. Diffractograms natural zeolite (ZA), H-Natural Zeolite H-(ZA), and TCA/Natural zeolite (TCA/ZA).

The acidity of the catalysts in this study using the gravimetric method by using ammonia as a base adsorbate to determine the acidity in the zeolite cavities (Table 1). The use of ammonia as adsorbate

alkaline due to the size smaller than pyridine then ammonia gas can be adsorbed on the outer surface and within the zeolite while pyridine only adsorbed on the outer surface of zeolite [10].

Table 1. The acidity of catalysts

Sample	Surface acidity (mol/g)
Natural zeolite	2.22×10^{-3}
H-Natural zeolite	2.42×10^{-3}
TCA/H-Natural zeolite	3.23×10^{-3}

Acidity measurement results indicate acidity TCA/Natural zeolite is greater than the H-Natural zeolite and acidity of H-Natural zeolite is greater than the Natural zeolite Trichloroacetic acid has a pair of free electrons that can accept an electron pair. Increased acid sites is possible because impregnated of trichloroacetic acid on the zeolite.

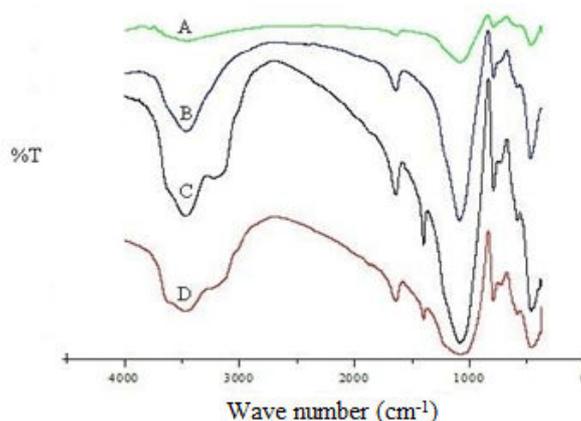


Figure 2. IR spectra (A) TCA/Natural zeolite (B) H-Natural zeolite (C) TCA/Natural zeolite+ammonia (D) H-Natural zeolite+ammonia

The presence of TCA in the catalysts was studied by FT-IR. Figure 2 shows the spectra of Natural zeolite, and TCA/natural zeolite. The carbonyl group stretching signal appeared at 1660 cm^{-1} . The bands assigned to stretching and bending due Cl-C bonds were observed at 830 cm^{-1} and 680 cm^{-1} [1].

3.2 Isomerization Reaction

The isomerization reaction of α -pinene was studied in heterogeneous phase by TCA/Natural zeolite as catalyst. Conversion of α -pinene to some compounds e.g camphene as major product and limonene, p-cimene, and terpinolene as minor product. Conversion of α -pinene and selectivity to camphene was determined in the following ways. Conversion (X) was defined here as moles of α -pinene converted per 100 moles of α -pinene feed. The selectivities to camphene (S) was defined as moles of camphene formed per 100 moles of α -pinene converted.

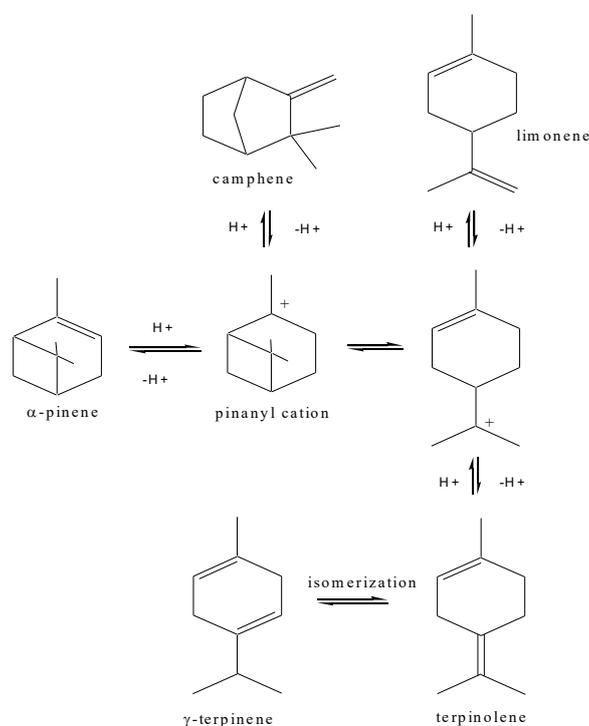
Table 2. Conversion α -pinene and selectivity to camphene with TCA/Natural zeolite catalyst

Catalysts	Reaction time (min)	320 W		480 W		640 W		800 W	
		X (%)	S (%)						
TCA/ H-Natural zeolite	15	3,47	33,97	12,26	27,73	23,25	28,26	29,83	22,90
	30	3,11	41,73	18,13	26,86	35,60	27,78	70,85	23,60
	45	5,40	33,88	29,75	26,35	66,88	26,30	88,48	19,43
	60	8,68	26,27	42,37	26,22	84,97	24,88	97,05	13,73
	90	13,46	22,43	76,01	24,26	98,99	16,90	98,85	6,59

X =Conversion of α -pinene, S = selectivity to camphene

Table 2 presents α -pinene conversion values (%X) and selectivities to camphene for the different treatments performed. When the TCA/Natural zeolite is exposed to a more severe power of microwave treatment, 320, 480, 640, 800 W the conversion increases but selectivities to camphene is decreases. The main product were camphene, α -terpinene, limonene, p-cimene, γ -terpinene, and terpinolene (Scheme 1).

The α -pinene isomerization can pass two parallel routes, leading to the formation of monocyclic products such as limonene, terpinolene, terpinene, p-cymene and bicyclic products, such as camphene. The first step in The reaction involves protonation of the double bond giving pinanyl cation. The second involves a Wagner-Meerwein type rearrangements of isobornyls and p-menthenyl cations giving camphene and others [11].



Scheme 1. Mechanism of the α -pinene isomerization with TCA/Natural zeolite

Heating with radiation microwave unlike conventional heating methods, heating with radiation microwave provides uniform heating throughout the reaction mixture so as to increase the temperature of the entire volume of the resulting reaction can be run faster [12].

Trichloroacetic acid (TCA) impregnated in natural zeolite can be used as a heterogeneous catalyst that can convert the α -pinene compound into its derivative compound. It is shown that α -pinene isomerization reaction with natural TCA / zeolite catalyst can produce camphene compound as main product with α -pinene conversion of 98.99% with selectivity 16.90%. The longer isomerization reaction time can increase the α -pinene conversion [1, 13].

4 Conclusion

TCA/Natural Zeolite was found a good catalyst for a production of camphene from α -pinene. The treatment microwave power has an important effect on the reaction activity on the selectivity to camphene, α -terpinene, limonene, p-cymene, terpinene, and terpinolene. The study on the effect microwave power (320 - 800 W) on conversion showed that 640W gives higher conversion (98.99%) and selectivity for camphene (16.90%) at room temperature.

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References

- [1] Avila M.C., Comelli N.A., Castellon E.R., Lopez A.J., Flores R.C., Ponzi E.N., Ponzi M.I., 2010. Study of Solid Acid Catalysis For The Hydration of α -pinene. *Journal of Molecular Catalysis*, 322(1-2): 106-112.
- [2] Bruno S.M., Pillinger M., Kuhn F.E., Goncalves I.S., Valente A.A., 2013. Isomerization of α -pinene oxide in the presence of methyltrioxorhenium (VII). *Catalysis Communications*. 35: 40-44.
- [3] Wijayati, N., Pranowo, dan Triyono, P., 2013. The Acid Catalyzed Reaction Of α -Pinene Over Y-Zeolite. *Indonesian Journal of Chemistry*, 13(1): 59-65.
- [4] Wijayati, N., T. Handayani, Supartono. 2017. Isomerization of α -pinene using Zirconium/Natural Zeolite Catalysts. *Asian Journal of Chemistry*. 29 (8) : 1705-1708.
- [5] Comelli N. A., Ponzi E. N., dan Ponzi M.I., 2006. α -Pinene Isomerization to Camphene Effect of Thermal Treatment on Sulfated Zirconia. *Chemical Engineering Journal*, 117(2): 93-99.
- [6] Wang J., W. Hua, Y. Yue, Z. Gao, 2010. MSU-S Mesoporous Material : An Efficient Catalyst For Isomerization of α -Pinene. *Bioresource Technology*, 101: 7224-7230.
- [7] Avila M.C., Ponzi M.I., dan Comelli N.A., 2015. Hydration of α -Pinene over Heteropoly Acid H3PW12O40 and H3PMo12O40. *Journal Chromatogr Sep Tech*, 6(7) : 1-6.
- [8] Reddy B.M., P.M. Sreekanth, V.R.Reddy, 2005. Modified Zirconia Solid Acid Catalysts For Organic Synthesis and Transformations. *Journal of Molecular Catalysis*, 225: 17-78.
- [9] Bhuiyan, Hossain, Mahmud and Al-Amin, 2011. Microwave-assisted Efficient Synthesis of Chalcones as Probes for Antimicrobial Activities. *Chemistry Journal*, 3(2): 2465-2479.
- [10] Flores-Holguin, N., A. Aguilar-Elguezal, L.M. Rodriguez-Valdez, 2008. Theoretical Study Of Chemical Reactivity Of The Main Species In The α -Pinene Isomerization Reaction. *Journal of Molecular Structure*, 854: 81-88.
- [11] Rachwalik, R., Olejniczak, Z., Jiao, J., Huang, J., Hunger, M., dan Sulikowski, B., 2007. Isomerization of α -Pinene Over Dealuminated Ferrite-Type Zeolites. *Journal Catal*, 252: 161-170.
- [12] Lidström, P., J. Tierney, B. Wathey, dan J. Westman, 2001. Microwave Assisted Organic Synthesis - a Review. *Tetrahedron*, 57: 9225-9283.
- [13] Wijayati, N., Pranowo, Jumina and Triyono, 2011. Synthesis Of Terpeneol From α -pinene Catalyzed By TCA/Y-Zeolite. *Indonesian Journal of Chemistry*, 11(3): 234-237.