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Catalytic activity of P₂O₅-natural zeolite on hydration reaction of turpentine into α -terpineol

Nanik Wijayati^{1,*}, N Hidayah¹, Sri Mursiti¹, Ella Kusumastuti¹

¹ Department of Chemistry, Faculty of Mathematics and Natural Sciences, State University of Semarang, D6 Building 2nd floor, Sekaran Campus, Gunungpati, Semarang, Indonesia

* Corresponding author: nanikanang@gmail.com

Abstract. Alpha-pinene compound can be derived into α -terpineol. The high content of this compound in turpentine oil will increase their selling value. Formation of α -terpineol by turpentine hydration reaction occurs with the aid of a catalyst. The catalyst can be derived from combination of homogenous and heterogeneous catalyst, namely phosphoric acid and activated natural zeolite (P₂O₅-natural zeolite). Characterization of P₂O₅-natural zeolite catalyst includes crystallinity analysis with XRD, functional group analysis with FTIR and acidity analysis with the gravimetric method. Hydration reaction was carried out in a batch reactor with variations of time (120, 240, 360, 480 minutes) and catalyst types (H₃PO₄, H-natural zeolite, P₂O₅-natural zeolite). Hydration reaction product were analysed using FT-IR, GC, and GC-MS. The result show that modification of catalyst by developing P₂O₅ is not significantly affected the crystalline structure of the H-natural zeolite. Hydration reaction reach optimum condition on the use of catalyst with H₃PO₄ 10% and P₂O₅-natural zeolite 40%, while reaction time 480 minutes' yield α -terpineol selectivity of 61,81% and 5,25% respectively.

1. Introduction

Pine sap requires processing so that it can be utilized further. Pine sap processing is intended to separate the rosin and turpentine oil. Turpentine oil in Indonesia contains of 65-85% α -pinene, 1-3% β -pinene, less 1% camphene, 10-18% 3-carene, and 1-3% limonene. A major component of turpentine oil is α -pinene compound. Turpentine oil can have a high selling value by synthesizing it derivative compounds, for example converting α -Pinene to α -Terpineol [1-6].

Alpha-terpineol is much utilized in the cosmetics industry, disinfectant, and deodorizer in the cleaning agent. Formation of α -terpineol is done through the hydration reaction with the help of homogeneous or heterogeneous catalysts. Use of homogeneous catalysts more quickly in the formation of reaction products, but has a weakness that is less friendly to the environment and separation products tend to be complicated because the catalyst is in a phase with reactants. Heterogeneous catalysts can be an alternative to overcome this, because it is a catalyst in a single phase with reactants and thus more environmentally friendly [7, 8].

The formation of α -Terpineol product begins with the formation of terpene hydrate when α -Pinene is reacted with dilute acids such as hydrochloric acid, nitric acid, and phosphoric acid. The selection of phosphoric acid as a catalyst because these compounds are classified as polyprotic acid which can provide two or more protons in ionization when hydration reaction takes place. The weakness of phosphoric acid tends to be more difficult to separate from their reactants because it is a homogeneous catalyst so it needs a heterogeneous catalyst namely zeolite [9, 10].



Natural zeolite is easy to be modified but it is necessary to activated first. Development of active natural zeolite was carried out on the active compound of phosphoric acid P_2O_5 , so that P_2O_5 - natural zeolite catalyst was formed. Characterization carried out on natural P_2O_5 -zeolite catalysts included analysis of crystal size, degree of crystallinity, and acidity. In addition, to investigate its catalytic activity, it was also examined the effect of the catalyst on the α -Terpineol product, and compare it with the turpentine hydration reaction using acid phosphorus.

2. Materials and Method

Materials used in this study include turpentine oil (from Perum Perhutani Unit I Central Java), natural zeolite (Malang), HF 1%, HCl 6 M, NH_4Cl 1 N, $AgNO_3$ 1%, ammonia, H_3PO_4 p.a. 85%, surfactant tergitol np-10, dichloromethane, anhydrous Na_2SO_4 , N_2 gas, distilled water and demineralised water. Instrumentation used include 100 mesh sieves, a series of reflux devices, Centurion Centrifuge (GP Series), Panalytical XRD (Version PW3050/60), FTIR PerkinElmer (Version 10.03.06), GC Agilent 6820 (Version A. 01. 03), and GC-MS Shimadzu (QP2010S).

Activation of natural zeolite was begun by destroying chunks of natural zeolite with mortar then sieved with a size of 100 mesh and then it is soaked with distilled water for 24 hours and dried in an oven at $120^\circ C$. Natural zeolite was also then soaked with a solution of HF for 30 minutes to remove the impurity and silica that is outside the framework of the zeolite and then with HCl for 30 minutes so that the process of dealumination occurs in zeolites. Natural zeolite then neutralized with demineralised water. The presence of Cl^- ion then removed by $AgNO_3$ test. Natural zeolite is then soaked with NH_4Cl and washed with demineralised water until neutral condition. The presence of Cl^- ion then removed again by $AgNO_3$ test. Natural zeolite is dried in an oven at $120^\circ C$ for 1 hour and calcined at $500^\circ C$ for 4 hours.

Preparation of H_3PO_4 catalyst is done by making a solution of H_3PO_4 10% in 10 mL volumetric flask, whereas the preparation of P_2O_5 -natural zeolite catalyst is done by making the P_2O_5 -natural zeolite catalyst with various concentration i.e. 10, 20, 40% with impregnation P_2O_5 through to H-natural zeolite. Each concentration of the catalyst is made by mixing phosphoric acid dissolved in 10 mL of demineralised water with 10 g H-natural zeolite. Impregnation is carried out at $80^\circ C$ until the solution mixed. The result of impregnation dried in an oven at $100^\circ C$ for 1 hour.

The water content in Turpentine oil is removed in advance by using Na_2SO_4 . Turpentine oil is analysed using GC and FT-IR. Turpentine oil which has been free of the water used for hydration reaction. Hydration reaction of turpentine is done in three-neck round bottom flask by mixing 8 mL of turpentine oil, 1.5 g surfactant tergitol np-10, and 2.5 mL of distilled water at $70^\circ C$ for 480 minutes. The catalyst used in the hydration reaction include H_3PO_4 , H-natural zeolite, and P_2O_5 -natural zeolite. A catalyst is added as many as 400 mg after the reaction temperature is reached. The results of the hydration reaction (the organic phase) are extracted using dichloromethane, neutralized with demineralised water, and anhydrous Na_2SO_4 is added to bind the remaining water and irrigated gas N_2 to evaporate residual solvent. Sample results are analysed using GC and the best hydration reaction results are analysed using GC-MS and FT-IR.

Analysis of the reaction products was performed by Gas Chromatography (GC) (Agilent 6820 Version A.01.03 equipped with flame ionization detector/FID). The column used was HP-5 (% phenyl methyl siloxane). The temperature of the column was adjusted to be $70^\circ C$ for 10 min and then increased to $280^\circ C$ by $5^\circ C/min$. The carrier gas used was helium (He) ($0.1 \mu L/min$ flow). The injection and detection temperatures were set to be 280 and $300^\circ C$, respectively and the split mode was 1/100. The various components were characterized by FT-IR and GC-MS instrument (QP2010S Shimadzu). The column used was Agilent DB-624: 30 m; id: 0.25 mm and the carrier gas used was helium. The temperature of the column was adjusted to be $60^\circ C$ for 5 min and then increased to $250^\circ C$ by $10^\circ C/min$. The FT-IR spectra of the heterogeneous catalyst were recorded on an FT-IR (PerkinElmer Version 10.03.06) in the 4000-450 cm^{-1} wave number range using KBr pellets. The determination of the structure of the heterogeneous catalysts was done by X-ray diffractometer using Panalytical (Version

PW3050/60) with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$, 400kV, 300mA). The range of scanning angle (2θ) was kept at 10-80 $^\circ$.

3. Results and Discussion

Catalyst characterization are performed to investigate properties of natural zeolite, active natural zeolite (H-natural zeolite), and P₂O₅-natural zeolite with concentrations of 10, 20, 40% include crystal size and crystallinity degree. Fig. 1 shows the type of mineral crystallinity of the zeolite.

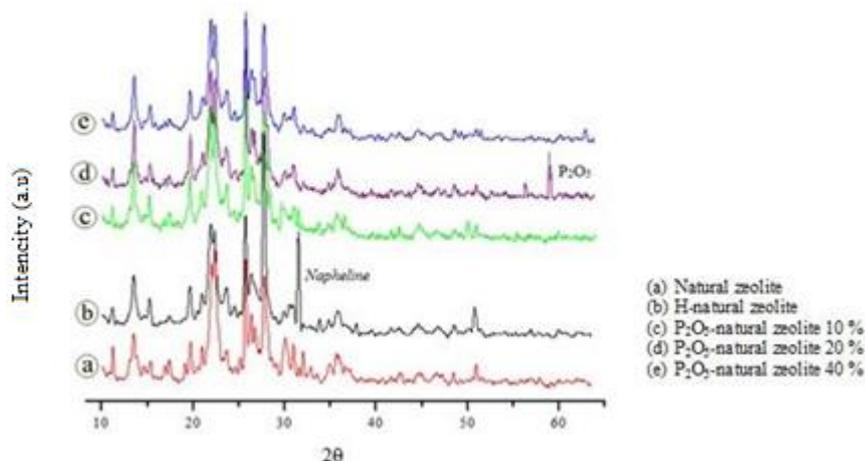


Figure 1. Diffractogram of the catalysts.

Diffractogram generated on each type of catalyst shows a sharp intensity on region $2\theta = 22.35^\circ$; 25.68° ; and 27.74° are characteristic mordenite zeolite type. This pattern of conformity in accordance with JCPDS no. 6-239 so it can be concluded that natural zeolite from Malang is including of mordenite zeolite type. The difference occurs on P₂O₅-natural zeolite 20% catalyst there is found of diphosphorus pentoxide (P₂O₅) on the surface of the zeolite is marked with detection of P₂O₅ on $2\theta = 59.06^\circ$ (JCPDS No. 22-1380). In H-natural zeolite catalyst there are sharp peaks on $2\theta = 31.92^\circ$ indicates a kind of other minerals of zeolite, that is napheline is detected on $2\theta = 30.98^\circ$ (JCPDS No. 19-1176).

Crystal size of catalyst that is based on a calculation using the Scherrer equation, shows that the P₂O₅-natural zeolite 40% catalyst has a larger crystal size i.e. 43.93 nm. This degree of crystallinity shows how large this material of catalyst and is said to be the crystalline. The highest degree of crystallinity is owned by P₂O₅-natural zeolite 10% catalyst i.e. 98.67%. High crystallinity is expected to have high catalytic properties, stable at high temperatures, high porosity, and free of impurity.

The acidity can be analysed to determine acid sites total in a material. In this study, acid sites total of the catalyst is determined quantitatively with the gravimetric method used ammonia as alkaline adsorbent. Molecule size of ammonia is smaller so it can interact with the site on the acid catalyst and finally ammonia is stronger adsorbed [7]. Impregnation of cation/metal on a material such as a zeolite can increase of acid sites total. The total acidity (ammonia) of the catalyst is presented in Table 1.

Table 1. Total acidity (ammonia) on the variation of catalyst type

Catalyst	The Acidity (mmol/g)
Natural zeolite	0.16
H-natural zeolite	0.48
P ₂ O ₅ -natural zeolite 10%	0.54
P ₂ O ₅ - natural zeolite 20%	0.75
P ₂ O ₅ - natural zeolite 40%	1.08

The highest acidity is on natural zeolite with modification i.e. P_2O_5 -natural zeolite 40% catalyst. This proves that natural zeolite with modification of P_2O_5 have larger acidity than natural zeolite catalyst without modification of P_2O_5 . The acidity increases with increasing concentration of P_2O_5 (Table 1). This acidity is an important factor in catalytic activity in the hydration reaction of turpentine.

Natural zeolite is activated at 500°C for 4 hours. Physical properties of H-natural zeolite and P_2O_5 -natural zeolite are white solids intangibles. The analysis of functional groups are performed on H-natural zeolite and P_2O_5 -natural zeolite 40% by using FTIR. On the H-natural zeolite and P_2O_5 -natural zeolite 40% catalyst indicate the presence of hydroxyl groups (-OH) at 3435 cm^{-1} and 3412 cm^{-1} , at peak absorption 794 cm^{-1} and 792 cm^{-1} showed a cluster of Si-O and absorption for peak 1092 cm^{-1} shows the vibration of Si-O-Si-O-Si/Al. Difference absorption peak shift is thought to result from the modifications made to the zeolite. The shift in the spectra of internal and external vibrations may explain the dealuminated zeolite.

Components in the turpentine oil (Fig. 2) include α -pinene (65-85%), β -pinene (1-3%), camphene (<1%), 3-carene (10-18%) and limonene (1-3%). Alphapinene compound is a major component in turpentine oil [2, 3, 6].

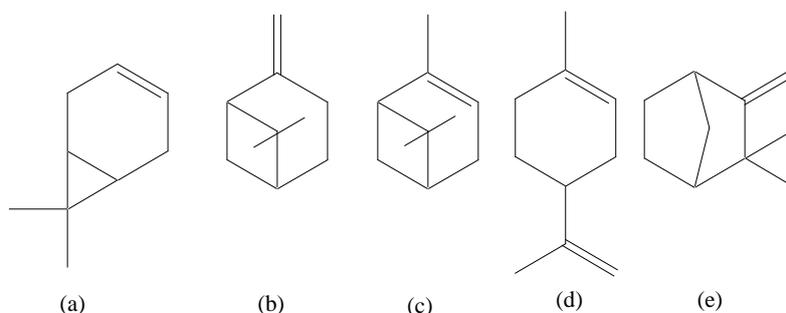


Figure 2. Structure of turpentine oil compound (a) 3-carene, (b) β -pinene, (c) α -pinene, (d) limonene, (e) camphene.

Derivates of α -pinene compound among others α -terpineol, 4-terpineol, and terpineol hydrate. The α -terpineol compound is a derivate of the α -pinene compound studied in this research through the hydration reaction of turpentine [1-6].

Based on results of the GC, α -pinene compounds content in turpentine oil of 80.89% that appear on retention time 3.702 minutes. These compounds reinforced with peaks characteristics of FT-IR characterization based on turpentine oil is detected on the wave number 2920 cm^{-1} indicating an alkane C-H absorption, 1651 cm^{-1} indicating an alkene C = C absorption, 1446 cm^{-1} indicating CH_2 absorption and 1382 cm^{-1} indicating CH_3 absorption.

Alphaterpineol product results of hydration reaction of turpentine with a variation of reaction time 2, 4, 6, and 8 hours for each type of catalyst. The type of catalyst used i.e. H_3PO_4 10%, H-natural zeolite, P_2O_5 -natural zeolite 10%, P_2O_5 -natural zeolite 20%, and P_2O_5 -natural zeolite 40%. Based on results of the GC, the highest concentration of α -terpineol is present on the reaction time 8 hour for all types of catalyst and optimum concentration of α -terpineol are present on H_3PO_4 10% catalyst. Following are results of GC on hydration reaction of turpentine by using H_3PO_4 10% catalyst with 8 hours of reaction time in Fig. 3.

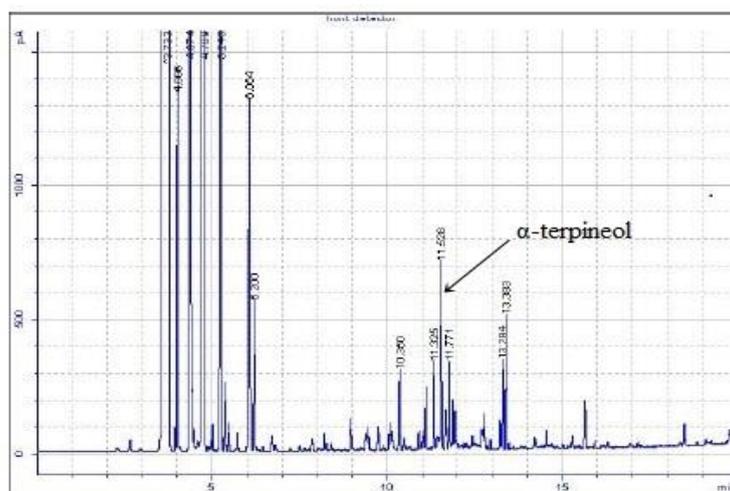


Figure 3. Chromatogram GC results of hydration reaction of turpentine on H_3PO_4 10% catalyst with 8 hours of reaction time.

The concentration of α -terpineol compound appears on retention time 11.697 minute of 20.43% and concentration of α -pinene left of 53.48%. The formation of the hydration reaction products is characterized by the occurrence of the concentration decrease α -pinene compound. The results of the conversion of α -pinene to produce α -terpineol optimum i.e. H_3PO_4 10% catalyst and P_2O_5 -natural zeolite 40% by comparison in Fig. 4.

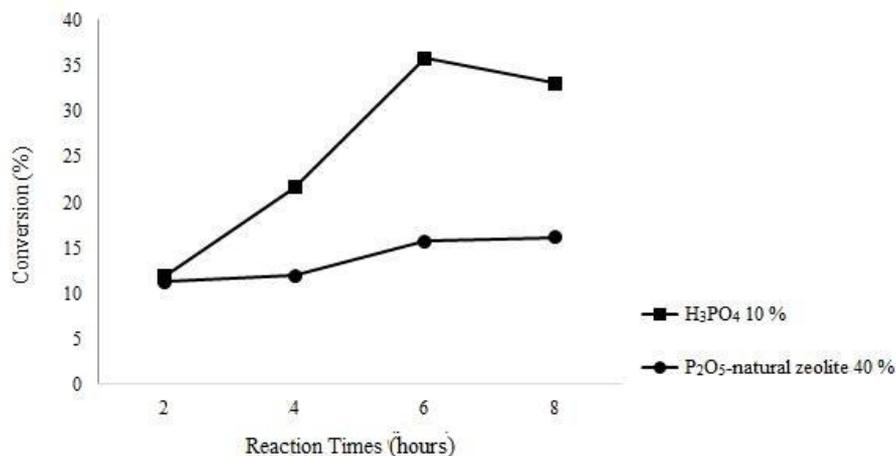


Figure 4. Conversion of α -pinene at H_3PO_4 10% and P_2O_5 -natural zeolite 40% catalyst with a variation of reaction time.

The increase of α -pinene conversion in each reaction times proves that concentration of α -pinene that is produced from hydration reaction is reduced. It indicates that of all α -pinene compounds, only some of them react into other compounds (become α -terpineol products).

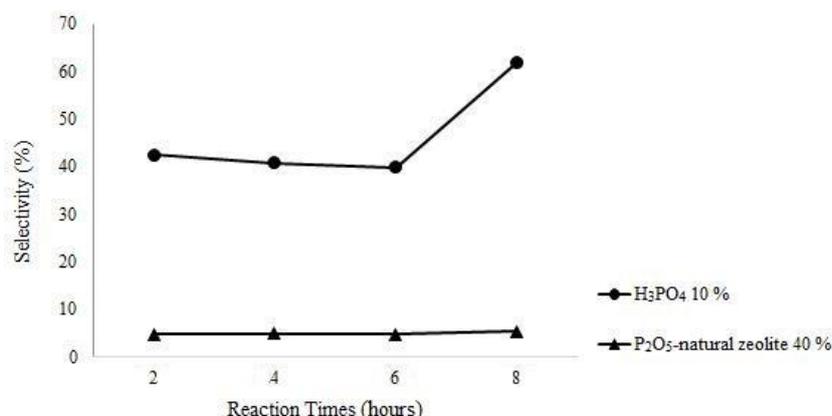


Figure 5. Selectivity of α -terpineol at H₃PO₄ 10% and P₂O₅-natural zeolite 40% catalyst with a variation of reaction time.

The conversion α -pinene to α -terpineol which increases causing selectivity of the α -terpineol product also tends to increase as presented in Fig. 5. The optimum selectivity of α -terpineol product is on reaction time 8 hours by H₃PO₄ 10% catalyst of 61.81%. The use of P₂O₅-natural zeolite 40% as catalyst produces α -terpineol with selectivity as 5.25%. Decreased of α -terpineol selectivity are caused by the formation of other compounds that become a by-product of the α -pinene isomerization include camphene, limonene, and terpinolene [1, 10].

The formation of α -terpineol compound is strengthened by using FT-IR characterization data that groups of O-H absorption of alcohol is a typical product of α -terpineol appeared in wave number 3401 cm⁻¹. The absorption peaks appear to be expected that the product of these reactions are alcohol compound. This is confirmed by the presence of strong absorption of C-O groups in wave number 1204 cm⁻¹ and the groups of alcohol compounds is reinforced with a widened absorption of O-H groups.

The GC-MS analysis is conducted on a sample of α -terpineol product with the highest selectivity. The sample is α -terpineol from reaction with H₃PO₄ 10% and P₂O₅-natural zeolite 40% as catalyst in reaction time 8 hours. The GC-MS analysis aims to find out the number of compounds, mass formula, structure formula, and the peak mass peak of compound result from hydration reaction of turpentine.

The mass spectrum of α -terpineol optimum from reaction with H₃PO₄ 10% as catalyst in reaction time 8 hours is presented in Fig. 6. Alpha-terpineol compound has a molecular mass of m/z mass spectra 154, but molecular ion with m/z 154 not detected by molecular ion mass spectrometer due to unstable, but it is estimated that the molecular ion fragment is detected next m/z 136, which is typical of a fraction of alcohol with the loss of one molecule of water.

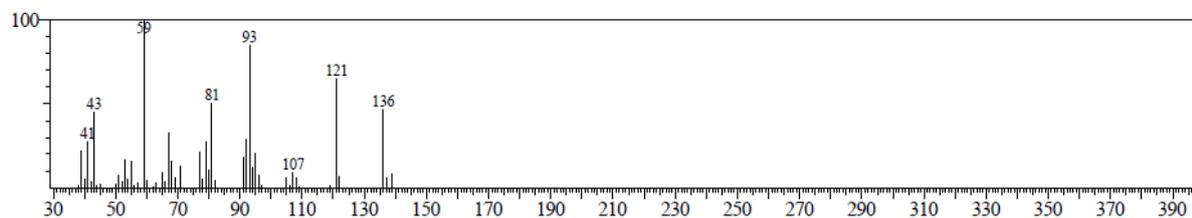


Figure 6. The mass spectrum of α -terpineol from hydration reaction with H₃PO₄ 10% as catalyst in reaction time 8 hours

Based in the GC-MS analysis on Fig. 7, there are differences between hydration reaction products with H₃PO₄ 10% as catalyst and P₂O₅-natural zeolite 40% as catalyst for 8 hours.

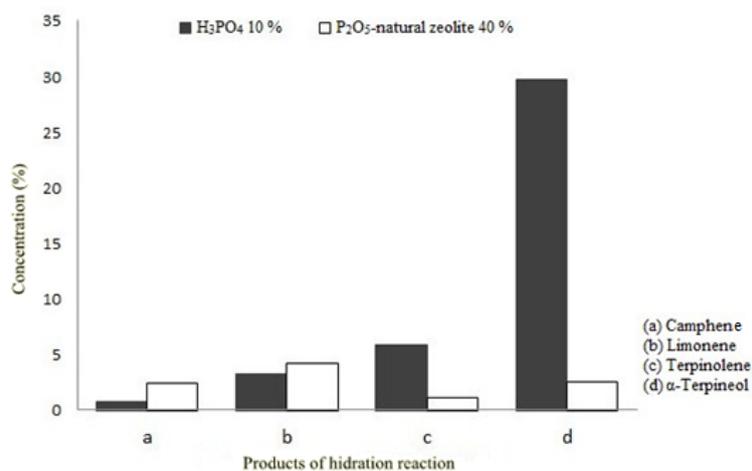


Figure 7. Comparison of hydration reaction product between use H₃PO₄ 10% as catalyst and P₂O₅-natural zeolite 40% as catalyst for 8 hours.

The highest concentration of 29.77% α -terpineol product is generated from hydration reaction with H₃PO₄ 10% as catalyst, while the use of P₂O₅-natural zeolite 40% as catalyst yields α -terpineol of 2.58%. The fact is reaction with P₂O₅-natural zeolite 40% as catalyst produces more other side products than reaction with H₃PO₄ 10% as catalyst. This is due to less the maximum performance of natural zeolite as a heterogeneous catalyst in the hydration reaction of turpentine. Activation of natural zeolite are insufficient so it loses their ability to interact with the catalyst in the reactants.

4. Conclusion

The catalytic activity of hydration reaction with H₃PO₄ 10% and P₂O₅-natural zeolite 40% as catalyst for reaction time 8 hours produces α -terpineol selectivity of 61,81% and 5,25% respectively.

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References

- [1] Wijayati N, Pranowo H D, Jumina J and Triyono T 2011 Synthesis of terpineol from α -pinene catalyzed by TCA/Y-Zeolite *Indones. J. Chem.* **11** 3 234-7
- [2] Wijayati N, Pranowo H D, Jumina J and Triyono T 2013 The acid catalyzed reaction of α -pinene over Y-zeolite *Indones. J. Chem.* **13** 1 59-65
- [3] Ávila M C, Comelli N A, Rodríguez-Castellón E, Jiménez-López A, Flores R C, Ponzi E and Ponzi M 2010 Study of solid acid catalysis for the hydration of α -pinene *J. Mol. Catal. A Chem.* **322** 1-2 106-12
- [4] Chibiryaev A, Yermakova A and Kozhevnikov I 2010 Chemical and phase equilibria calculation of α -pinene hydration in CO₂-expanded liquid *J. Supercrit. Fluids* **51** 3 295-305
- [5] Yadav M K, Patil M V and Jasra R V 2009 Acetoxylation and hydration of limonene and α -pinene using cation-exchanged zeolite beta *J. Mol. Catal. A Chem.* **297** 2 101-9
- [6] Mochida T, Ohnishi R, Horita N, Kamiya Y and Okuhara T 2007 Hydration of α -pinene over hydrophobic zeolites in 1, 4-dioxane-water and in water *Microporous Mesoporous Mater.* **101** 1-2 176-83
- [7] Wijayati N, Handayani T and Supartono 2017 Isomerization Reaction of α -Pinene Using Zirconia/Natural Zeolite Catalysts *Asian J. Chem.* **29** 8 1705-8
- [8] Liu S-W, Yu S-T, Liu F-S, Xie C-X, Li L and Ji K-H 2008 Reactions of α -pinene using acidic

- ionic liquids as catalysts *J. Mol. Catal. A Chem.* **279** 2 177-81
- [9] Avila M, Ponzi M and Comelli N 2015 Hydration of α -Pinene over Heteropoly Acid H₃PW₁₂O₄₀ and H₃PMo₁₂O₄₀ *J. Chromatogr. Sep. Tech.* **6** 1-6
- [10] Li Y, Wang C, Chen H, Hua W, Yue Y and Gao Z 2009 Isomerization of α -Pinene Over Porous Phosphate Heterostructure Materials: Effects of Porosity and Acidity *Catal. Lett.* **131** 3-4 560-5