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Activity and selectivity of Ni/ beta zeolite and Cu/beta zeolite catalysts on citronellal cyclization reaction from citronella oil

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Abstract. Isopulegol is an intermediate compound for synthesis some fine chemical and used in the pharmaceutical, soap and tooth paste industry. Conversion of citronellal to isopulegol in catalysed cyclization reaction has been investigated. Isopulegol can be produced by using cyclization reaction of citronellal with Ni/beta zeolite and Cu/beta zeolite catalysts. Citronellal has been isolated from citronella oil by fractional distillation under reduced pressure. The structure of product were analyzed by using GC, GC-MS and FTIR. The catalysts were prepared by using impregnation method and characized by using XRD and SAA instruments. Citronellal cyclization was carried out at 180°C for 4 hour. Based on GC and GC-MS analysis, it was shown that concentration of isolated citronellal of 84.26%. XRD analysis of catalysts showed that the metals were impregnated with beta zeolite. Citronellal cyclization using Cu/beta zeolite catalyst produces 69.31% isopulegol and Ni/beta zeolite catalyst produce isopulegol at 29.68%. The Cu/beta zeolite catalyst has an activity of 90.20% and selectivity of 80.98%. The activity of Ni/beta zeolite catalyst of 42.53% with selectivity of 76.60%. These results indicate that Cu/beta zeolite catalyst is better than Ni/beta zeolite in citronellal cyclization.

1. Introduction

Isopulegol is an intermediate compound to synthesis some fine chemical and usually used in the pharmaceutical, soap and toothpaste industry [1]. Isopulegol is very expensive because to get the compound, it is necessary to change compounds in various stages which are quite long. Citronellal is one of the compounds to produce isopulegol.

Citronellal is one of the biggest components in citronella oil, which is 28-45% [2][3]. Citronellal has two active groups, the C=O carbonyl group and the C6=C7 double bond, and one asymmetric (chiral) C atom. The existence of one chiral carbon atom causes the citronellal to have two prochiral carbon atoms which can be converted to asymmetric centers in isopulegol intermediates [4]. The conversion of citronellal into isopulegol is carried out through a cyclization reaction.

The cyclization reaction can be conducted in the presence of an acid catalyst with a strong Lewis acid site. Lewis acids are used in the cyclization reaction are ZnBr₂, ZnCl₂, ZnI₂. The disadvantage of using this homogeneous catalysts are several obstacles in handling, storing, and using it, which takes a long time. The potential acid catalyst in this reaction is beta zeolite because it has large pores and surface area, stable heating, and has structures with high silica content [5]. Acidity of Lewis acid site in beta zeolite is lower than Bronsted acid site. Therefore, it can be developed of active metal to replace the

Bronsted acid site with a Lewis acid site in the beta zeolite. Some solid acid catalysts also reorted activity and selectivity on the cyclization of citronellal to isopulegol [6-9].

Ni and Cu metals are usually used as Lewis acid sites in catalysts because they have good activity and selectivity in a reaction, especially to the C=O carbonyl group [10]. Besides, Ni and Cu metals are easy to obtain, so the price is cheap. The addition of a metal in beta zeolite can increase catalyst selectivity in the cyclization reaction. Citronella cyclization to isopulegol with Cu/ZnBr₂/γ-Al₂O₃ catalyst and produce isopulegol a 2.53% [11]. The Sn/beta zeolite catalyst has an selectivity of 85% [12]. In this research will be compared the greatest activity and selectivity of catalysts in the conversion of citronellal to isopulegol.

2. Method

2.1. Isolation and Identification of Citronellal from Citronella Oil

Isolation of Citronellal from citronella oil was carried out by using fractional distillation under reduced pressure. Citronella oil a 250 ml was put into a bottom flask and the distillation device was adjusted. The pressure used for distillation is set at 29.9-30.1 mmHg. The distillate is collected in several fractions based on differences in boiling points. The results of the distillate in various fractions were analyzed by GC, GC-MS, and FTIR.

2.2. Preparation and Characterization of Ni/beta zeolite and Cu/beta zeolite Catalysts

Ni/beta zeolite and Cu/beta zeolite catalysts were prepared by using impregnation's method [13]. Beta H-Zeolite is activated by heating for 2 hours at 150°C. Beta H-zeolites are immersed in Ni(NO₃)₂ and Cu(NO₃)₂ dissolved. The mixture is heated at 40°C and stirred using a magnetic stirrer for 3 hours. The Ni/beta zeolite and Cu/beta zeolite slurries were dried at 110°C for 2 hours and calcined at 500°C for 4 hours. Catalysts were reduced with H₂ gasses at 180°C for 4 hours and analyzed by using XRD and SAA instruments.

2.3. Citronella Cyclization

The citronellal cyclization process were conducted in a glass column. The catalysts and citronellal were added to a glass column and heated (oil bath) at 180°C for 4 hours. The reaction results were centrifuged and analyzed by using GC, GC-MS and FTIR.

3. Results and Discussion

3.1. Citronellal Isolation from Citronella Oil

Citronella oil is an essential oil whose components have adjacent boiling points so that citronellal isolation process is carried out using a pressure reduction distillation method. The use of reduction pressure is intended so that citronellal can evaporate faster than normal boiling points. Fractional distillation of citronella oil was produced three fractions, the second fraction has a citronellal aroma stronger than the other two fractions. The results of GC analysis of isolated citronellal and citronella oil can be shown that the citronellal content in the second fraction increased to 84.26% followed by a decrease in other components. Based on the chromatogram showed that the second fraction was citronellal. This was proven by FTIR which showed a functional group in the citronellal. The absorption band shows the stretching vibrations of the groups contained in the citronellal. The IR spectrum shows aliphatic C-H vibrations in the area of 2915 cm⁻¹. Vibration stretching from C-H aldehydes in the area of 2707 cm⁻¹ to 2871 cm⁻¹. The C=O carbonyl group is in the absorption area of 1724 cm⁻¹, while the vibrations of the alkene C=C are in the region of 1635 cm⁻¹. In the absorption region, 1454 cm⁻¹ indicates the presence of -CH₂- group and -CH₃ group in the absorption area of 1379 cm⁻¹.

3.2. Ni/beta zeolite and Cu/beta zeolite catalyst

Ni/beta zeolite and Cu/beta zeolite catalysts were prepared by using impregnation method. Ni/beta zeolite and Cu/beta zeolite catalysts were analyzed by using X-Ray Diffraction (XRD) and SAA instruments. The results of the XRD analysis can be seen in Figure 1.

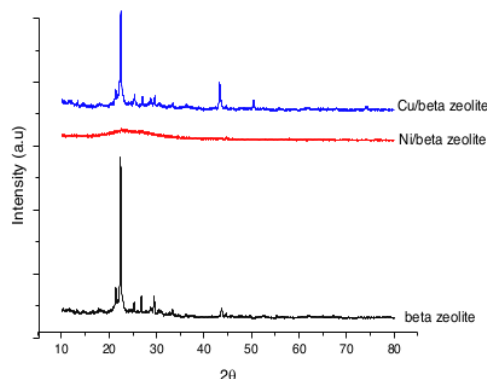


Figure 1. Diffractogram of Beta Zeolite . Ni/Beta Zeolite, and Cu/Beta Zeolite

Figure 1. shows that the vertical axis (x) is the intensity of the X-ray and the horizontal axis (y) is the scattering angle of 2θ . Based on the results of three diffractograms, it can be seen that there is a sharp peak, widening the peak and decreasing the relative intensity of the angle of 2θ . In h-zeolite, beta shows peaks at $2\theta = 21.42^\circ, 22.44^\circ, 25.30^\circ, 26.79^\circ,$ and 29.52° . Based on the results of JCPDS (Combined Powder Diffraction Standards Committee), this peak is the characteristic peak of beta zeolite.

Beta zeolite that has been impregnated by Ni and Cu metals produce new peaks and don't experience significant changes. These results indicate that beta zeolite has a structure with high stability despite calcination and reduction during the impregnation process. Based on the diffractogram in Figure 3. shows the difference in the peak after the addition of Ni and Cu metals.

Cu/beta zeolite catalyst there is a decrease in intensity which indicates that the Cu metal has been absorbed in the beta zeolite. This is supported by the appearance of a new peak at $2\theta = 43.27^\circ; 50.49^\circ; 74.13^\circ$ which is the peak of the Cu metal [14]. Peaks shows that the material being tested is crystal. The peaks of Ni/beta zeolite catalyst don't exist, so the material may be mass because the structure is amorphous. The appearance of Ni metal peaks appears at $2\theta = 44.66^\circ$. The presence of a lump in the beta Ni/zeolite indicates damage to beta zeolite because Ni metal was impregnated. Damage of beta zeolite make the effective pore size of beta Ni/zeolite as a catalyst was smaller.

Ni/beta zeolite and Cu/beta zeolite catalysts were analyzed by SAA instruments to know the surface area of catalysts. The SAA results of catalysts can be seen in Table 1.

Table 1. Surface Area of Catalysts

Catalysts	Surface Area (m^2/g)
Beta Zeolite	443.974
Ni/Beta Zeolite	6.811
Cu/Beta Zeolite	237.731

Table 1 shows that the surface area of beta zeolite has decreased after Ni and Cu metals were impregnated. The decrease in surface area of beta zeolite shows that the Ni and Cu metals have been distributed and fill in some pores of beta zeolite. Impregnation is a method to expand the surface area which it can increase the activity of catalysts. Metals were impregnated in beta zeolite will reduce surface area of beta zeolite but it can increase the reactivity on the metals side.

3.3. Cyclization of Citronellal.

Citronellal has two active groups, the C=O carbonyl group and the C6=C7 double bond, and one asymmetric (chiral) C atom. The existence of one chiral carbon atom causes the citronellal to have two prochiral carbon atoms which can be converted to asymmetric centers in isopulegol intermediates. GC results between citronellal cyclization with beta Ni/zeolite catalyst and Cu / zeolite can be seen in Figure 2. Based on the results of GC and GC-MS shows that the results of citronella cyclization are isopulegol compounds.

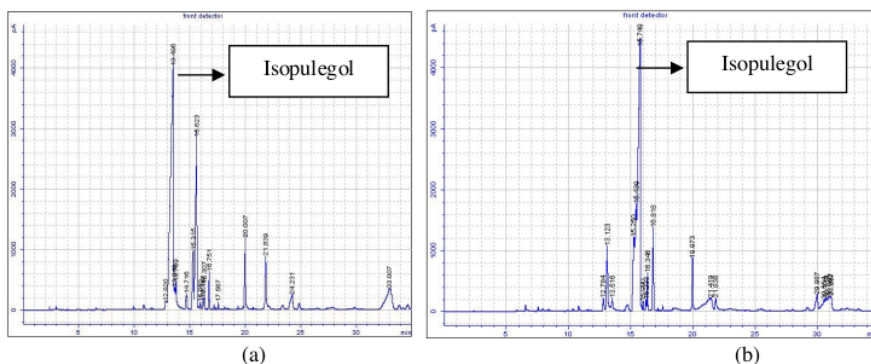


Figure 2. Chromatogram of Cyclization Reaction with (a) Ni/Beta Zeolite (b) Cu/Beta Zeolite

Citronella cyclization with Ni/beta zeolite and Cu/beta zeolite catalysts in this study can be said to be successful. This can be seen in Figure 2 which shows there are of new peaks at retention times 15.623 (2a) and 15.749 (2b) followed by a decrease in the citronellal peak at the retention time 13. Citronellal cyclization catalyzed by Ni/beta zeolite produced a product of 29.68% and Cu/beta zeolite catalyst produced a product of 69.31%. Determination activity and selectivity of catalysts in the citronellal cyclization can be seen on quantity of isopulegol was produced, citronellal conversion, and selectivity of isopulegol in Table 2.

Table 2. Determination of Catalysts on Citronellal Cyclization

Catalysts	Citronellal Conversion	Quantity of Pulegol	Selectivity of Isopulegol
Ni/Beta Zeolite	42.53%	29.68%	76.60%
Cu/Beta Zeolite	90.20%	69.31%	80.98%

Table 1 shows that the activity and selectivity of Ni/beta zeolite catalyst is better than Ni/beta zeolite. Relative activities of catalysts are shown by its conversion (mol%) [15]. The low yield of citronellal cyclization with Ni/beta zeolite catalyst because Ni/beta zeolite catalyst are in bulk with an amorphous structure which results in a low effect on the pore size of the catalyst [16].

The results of the cyclization were analyzed by FTIR to determine the isopulegol functional group. The IR spectrum can be seen in Figure 2.

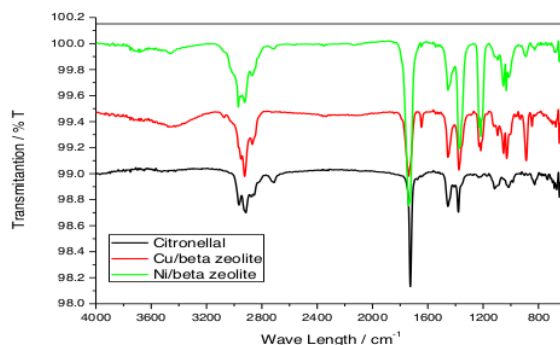


Figure 3. IR Spectrum of Catalytic Citronellal Cyclization product

Based on the IR spectrum in Figure 3 there is a difference between the results of citronellal and citronellal cyclization. In the absorption area 3447 cm^{-1} there is a stretching vibration from the -OH group. The stretching vibration of the aliphatic C-H in the absorption area is $2923\text{ to }2868\text{ cm}^{-1}$. In the absorption area 1737 cm^{-1} shows the stretching vibration of C=O carbonyl, the absorption band 1646 cm^{-1} shows the stretching of C=C alkene, the absorption band 1454 cm^{-1} there is a stretching vibration of CH_2 , the absorption band 1369 cm^{-1} indicates the presence of CH_3 vibration and C-O vibration in the absorption area of 1216 cm^{-1} .

Citronellal cyclization reaction using Ni/beta zeolite and Cu/beta zeolite catalysts produce (-)-isopulegol and (+)-neoiso(iso)pulegol. The results of citronellal cyclization can be seen in Table 3.

Table 3. GC-MS Chromatogram of Citronellal Cyclization

Retensi Time	Area (%)	Name
16.764	7.44	Citronellal
19.965	18.72	Neoiso(iso)pulegol
20.310	67.47	(-)-Isopulegol
22.373	4.15	Neoiso(iso)pulegol

4. Conclusion

The Cu/beta zeolite catalyst has better activity and selectivity compared to Ni/ beta zeolite on citronellal cyclization into isopulegol. The results of citronellal cyclization with beta Cu/beta zeolite catalyst for 4 hours were able to produce a product (-)-isopulegol of 69.31% and catalyst Ni/beta zeolite of 29.68%. Cu/beta zeolite catalyst has 90.20% activity and 80.98% selectivity. While activity of Ni/beta zeolite catalyst was 42.53% with a selectivity of 76.60%. These results indicate that Cu/beta zeolite catalyst is better than Ni/ beta zeolite in citronellal cyclization.

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