

One-Pot Transformation of (*R*)-(+)-Citronellal over a Bifunctional Ni/ZnBr₂/β-Zeolite Catalyst

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Abstract

The transformation of (*R*)-(+)-citronellal to isopulegols and menthols in a one-pot reaction was improved using a zeolite catalyst. The one-pot transformation of (*R*)-(+)-citronellal was studied through a Ni/ZnBr₂/β-zeolite catalyst. The Ni/ZnBr₂/β-zeolite catalyst was prepared by impregnating 15% ZnBr₂ (w/w) and 15% Ni (w/w) on β-zeolite. The addition of Ni to the ZnBr₂/β-zeolite catalyst resulted in a useful bifunctional catalyst that combined a high rate of cyclization of citronellal to isopulegols over ZnBr₂ sites and subsequent hydrogenation to menthol over Ni sites. These catalysts were characterized using X-ray diffractometer (XRD) and scanning electron microscope-energy dispersive X-ray spectrometer (SEM-EDX). Catalytic reactions were carried out at 120 °C with magnetic stirring under a 1 atm nitrogen atmosphere for 1 h (cyclization reaction) and maintained under a 1 atm hydrogen atmosphere for 4 h (hydrogenation reaction). Products of the reaction were measured using gas chromatography-mass spectrometer (GC-MS) and gas chromatography (GC). The results showed that the Ni/ZnBr₂/β-zeolite catalyst can transform (*R*)-(+)-citronellal to isopulegols and menthols in a one-pot transformation, with a selectivity to isopulegols of 73.8% and selectivity to menthols of 6.40%.

Abstrak

Transformasi Satu Tahap (*R*)-(+)-Sitronelal Menggunakan Katalis Dwi Fungsi Ni/ZnBr₂/β-zeolit. Transformasi satu tahap (*R*)-(+)-sitronelal menjadi isopulegol dan mentol dapat dilakukan dengan katalis berbasis zeolit. Pada penelitian ini dilakukan transformasi satu tahap (*R*)-(+)-sitronelal menggunakan katalis Ni/ZnBr₂/β-zeolit. Katalis Ni/ZnBr₂/β-zeolit dibuat dengan metode impregnasi 15% ZnBr₂ (b/b) dan 15% Ni (b/b) pada β-zeolit. Penambahan Ni pada katalis ZnBr₂/β-zeolit bertujuan untuk membentuk katalis dwi fungsi yang menggabungkan situs ZnBr₂ untuk siklisasi sitronelal menjadi isopulegol yang dilanjutkan hidrogenasi isopulegol membentuk mentol melalui situs Ni. Katalis dikarakterisasi menggunakan *X-Ray diffractometer* (XRD) dan *scanning electron microscope-energy dispersive X-ray spectrometer* (SEM-EDX). Reaksi katalitik (*R*)-(+)-sitronelal dilakukan pada temperatur 120 °C dengan pengadukan magnet dalam kondisi atmosfer gas nitrogen selama 1 jam (reaksi siklisasi) kemudian dilanjutkan pada atmosfer gas hidrogen selama 4 jam (reaksi hidrogen). Produk reaksi dianalisis menggunakan kromatografi gas-spektrometer massa (KG-SM) dan kromatografi gas (KG). Hasil penelitian menunjukkan bahwa katalis Ni/ZnBr₂/β-zeolit dapat mentransformasi (*R*)-(+)-sitronelal menjadi isopulegol dan mentol dalam satu tahap, dengan selektivitas terhadap isopulegol sebesar 73,8% dan selektivitas terhadap mentol sebesar 6,40%.

Keywords: citronellal, isopulegols, menthols, one-pot transformation, zeolite catalyst

1. Introduction

Citronellal (3,7-dimethyl-6-octen-1-al) **1** in citronella oil from *Cymbopogon winterianus* Jowitt is a monoterpene aldehyde compound with unsaturated groups [1]. The citronellal structure has two active groups, that is carbonyl group (C₁) and double bond (C₆=C₇). In addition, citronellal also has one asymmetric (chiral)

carbon atom on C₃. The existence of a chiral carbon atom means that citronellal has two prochiral carbon atoms that can be converted into a center of asymmetry in isopulegol intermediates. The transformation products of citronellal are shown in Figure 1. The most important transformation product is menthol, which has many uses in industry.

Menthol can be synthesized from citronellal through a two-step reaction, that is, cyclization of citronellal to isopulegol **2** over an acid catalyst and further hydrogenation to menthol **3** over a metal catalyst. Cyclization of citronellal to isopulegol is an important step in the synthesis of menthol. This cyclization reaction is carried out in the presence of an acid catalyst. Bronsted acid can increase the rate of isomerization of citronellal, but the rate of formation of (-)-isopulegol **2a** is very low [2]. Nakatani and Kawashima [3] reported that Lewis acids (which act as an electron pair acceptor) such as ZnBr_2 , ZnCl_2 , and ZnI_2 can serve as a cyclization catalyst of citronellal. ZnBr_2 in solution and in anhydrous solids has yields of isopulegol of up to 92% with a selectivity of 94%.

The use of the anhydrous solid of ZnBr_2 as an acid catalyst in the cyclization of citronellal involves difficulties in handling, storage, and the necessity of carrying out many time consuming steps; moreover, it cannot be regenerated. Conversely, the synthesis of heterogeneous catalysts is easy to handle and provides high stereoselectivity in the desired product; this can be used as a strategic tool for the isopulegol synthesis process. The impregnation of ZnBr_2 on supported catalysts has been reported. Here, the $\text{ZnBr}_2/\text{SiO}_2$ catalyst gave stereoselectivity to (-)-isopulegol of 86% [4], $\text{ZnBr}_2/\gamma\text{-Al}_2\text{O}_3$ with 5% ZnBr_2 gave stereoselectivity to (-)-isopulegol of 64.29% [5], and the $\text{ZnBr}_2/\text{C16-HMS}$ catalyst gave stereoselectivity to (-)-isopulegol of 87% [6].

Impregnating ZnBr_2 on zeolite beta (β -zeolite) as a supported catalyst has not been widely reported. β -Zeolite is an acid catalyst potential because it has large pores and forms a three-dimensional framework structure

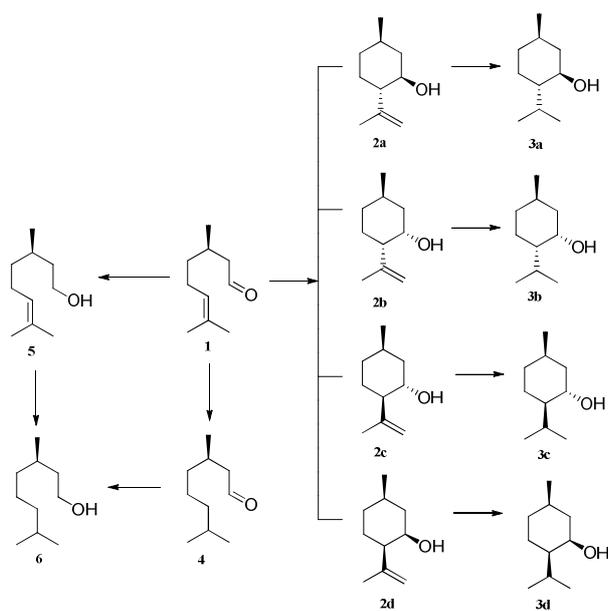


Figure 1. Transformation Products of (R)-(+)-Citronellal

with high silica content [7]. The number of Bronsted acid sites on β -Zeolite is higher than Lewis acid sites [8]. Strong Lewis acids are stereoselective and play a role in the mechanism of the formation of isomer (-)-isopulegol [9]. This has encouraged researchers to make an effort to replace Bronsted acid sites with Lewis acid sites by impregnating active metal. In previous studies, the use of β -zeolite as a supported catalyst to convert citronellal to menthol has been widely reported. For example $\text{Ni}/\text{Zr}/\beta$ -zeolite catalyst [10], Pt/β -zeolite catalyst [11], Sn/β -Zeolite catalyst [12], and Ir/β -Zeolite catalyst [13], which they can act as bifunctional catalyst which yields menthol **3a** in single step reaction.

The hydrogenation reaction of isopulegol to menthol requires metal catalysts such as Ni, which can accelerate the rate of reaction. Ni metal exhibits high activity in the processes of cracking, isomerization, hydrogenation, and ring opening of hydrocarbons [14]. Various studies have reported the use of Ni metal as an active metal on catalyst for the hydrogenation reaction of isopulegol to menthol, they are Ni/β -zeolite catalyst [15], $\text{Ni}/\text{MCM-41}$ catalyst [10], NiZrS catalyst [16], and $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalyst [17].

In this study, we tried to improve the transformation of (R)-(+)-citronellal in a one-pot reaction using a bifunctional catalyst to simplify the process of synthesizing menthol. The one-pot transformation of citronellal is more efficient, while separation of the catalyst from a mixture of products is easier. The process is also environmentally friendly. Here, we report our study on the one-pot transformation of (R)-(+)-citronellal over the $\text{Ni}/\text{ZnBr}_2/\beta$ -zeolite catalyst.

2. Methods

Materials. General remarks: β -Zeolite (Zeolite 940NHA, *Tosoh*, $\text{BET} = 580 \text{ m}^2/\text{g}$, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 37 \text{ mol/mol}$, cation type = NH_4), $\text{ZnBr}_2 \cdot 2\text{H}_2\text{O}$ (*Merck*), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (*Merck*), methanol (*Merck*), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (*Merck*), (R)-(+)-citronellal (96%) (*Merck*), gas nitrogen (*PT. Tira Austenite Tbk*), and gas hydrogen (*PT. Tira Austenite Tbk*).

Instrumentation. X-Ray diffractometer (XRD, Panalytical X'Pert Pro), scanning electron microscope-energy dispersive X-ray spectrometer (SEM-EDX TM3000, Hitachi High-Tech), gas chromatograph (GC HP 5890 series II, column = CBP-1), and gas chromatograph-mass spectrometer (GC-MS-QP2010S, column = DB-1, Shimadzu).

Catalyst preparation. The $\text{Ni}/\text{ZnBr}_2/\beta$ -zeolite catalyst was prepared by adding the ZnBr_2/β -zeolite catalyst to a methanol solution containing 15% Ni (w/w) from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt. The solution was stirred at room temperature for 24 h. After impregnation, the solvent

was slowly removed. The catalyst was dried at 120 °C for 2 h, and then calcined under nitrogen flow at 500 °C for 3 h. Before catalytic testing, the catalyst was reduced under hydrogen flow at 500 °C for 2 h.

The ZnBr₂/β-zeolite catalyst was prepared by adding the support β-zeolite to a methanol solution containing 15% Zn (w/w) from ZnBr₂·2H₂O salt. The solution was stirred under room temperature for 24 h. After impregnation, the solvent was slowly removed. The catalyst was dried at 120 °C for 2 h, and then calcined under nitrogen flow at 400 °C for 4 h.

Catalyst characterization. XRD patterns were recorded using Panalytical X'Pert Pro, operated at 40 kV and 30 mA, using Cu Kα radiation with λ₁ = 1.54060 Å and λ₂ = 1.54443 Å. Samples were scanned at 10° 2θ to 100° 2θ using a step size of 2θ = 0.02 and a time per step of 0.5 seconds; the diffractograms were recorded. Morphology catalysts and the contents of catalysts were obtained using an SEM-EDX TM3000 (Hitachi High Tech), and the samples were coated on the carbon grid.

Catalytic testing. The catalytic tests were performed at 120 °C in a modified catalytic reactor flask. The Ni/ZnBr₂/β-zeolite catalyst (0.5 g) was added to the flask and then the substrate (+)-citronellal ±3 ml was added. Catalytic reactions were carried out using magnetic stirring under a 1 atm nitrogen atmosphere for 1 h and maintained under a 1 atm hydrogen atmosphere for 4 h. Samples were taken regularly from the reactor at 30, 60, 120, 180, 240, and 300 min of reaction time. The catalyst and reaction mixture were separated by centrifugation at 5000 rpm for 30 min.

Product characterization. The reaction mixture was analyzed by GC using a 100% dimethyl polysiloxane (CBP 1, 30 m, 0.25 mm i.d.) capillary column. Reaction products were identified through their MS (HP 597 series, DB 1 [100% dimethyl polysiloxane], 30 m, 0.25 mm, i.d.).

3. Results and Discussion

Characterization of the catalysts. Figure 2 shows the XRD patterns of the Ni/ZnBr₂/β-zeolite catalyst, ZnBr₂/β-zeolite catalyst, and β-zeolite. All investigated catalysts presented the characteristic XRD peaks of crystallite β-zeolite (2θ = 21.5°, 22.5°, 29.5°, and 43.6°), indicating that these catalysts possess the skeletal structure β-zeolite. It must be assumed that amorphous ZnBr₂ and Ni are present on the surface of β-zeolite in the form of a mono- or multilayer [18]. In the XRD pattern of Ni/ZnBr₂/β-zeolite, the absence of the diffraction peak of NiO can be observed in Figure 2(c); it can be suggested that NiO obtained from the

calcination step were converted become Ni(0) in the reduction step.

SEM coupled with the EDX of the catalysts was also performed. SEM micrograph pictures of the Ni/ZnBr₂/β-zeolite catalyst showed that the morphological catalyst is different with ZnBr₂/β-zeolite catalyst; the presence of Ni metal appeared as white spots (Figure 3). The crystal showed the truncated square bipyramidal structure, typical crystal of β-zeolite [19]. For the EDX analysis, the ZnBr₂/β-zeolite catalyst showed that Br was still present (Figure 4).

We did not separate the isomers of isopulegols, so we used the general term “isopulegols.” The selectivity of the product reactions and conversion of citronellal were calculated using the following formulas [5]:

$$\text{Conversion of citronellal} = \frac{A - B}{A} \times 100\% \quad (1)$$

$$\text{Selectivity of isopulegols} = \frac{\Sigma \text{isopulegol}}{A - B} \times 100\% \quad (2)$$

$$\text{Selectivity of menthols} = \frac{\Sigma \text{menthol}}{A - B} \times 100\% \quad (3)$$

Note = A: initial citronellal; B: citronellal unreacted.

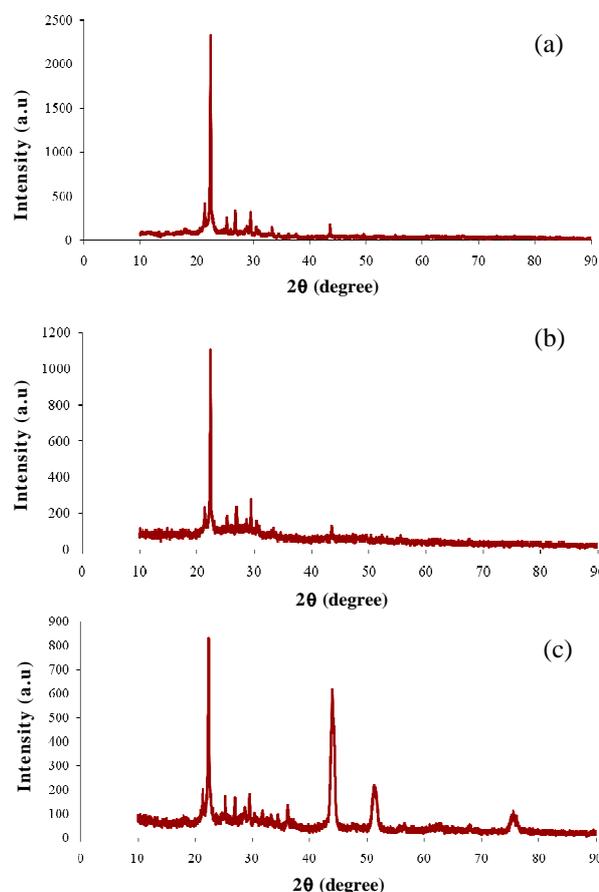


Figure 2. XRD Patterns for Catalysts (a) β-zeolite, (b) ZnBr₂/β-zeolite, and (c) Ni/ZnBr₂/β-zeolite

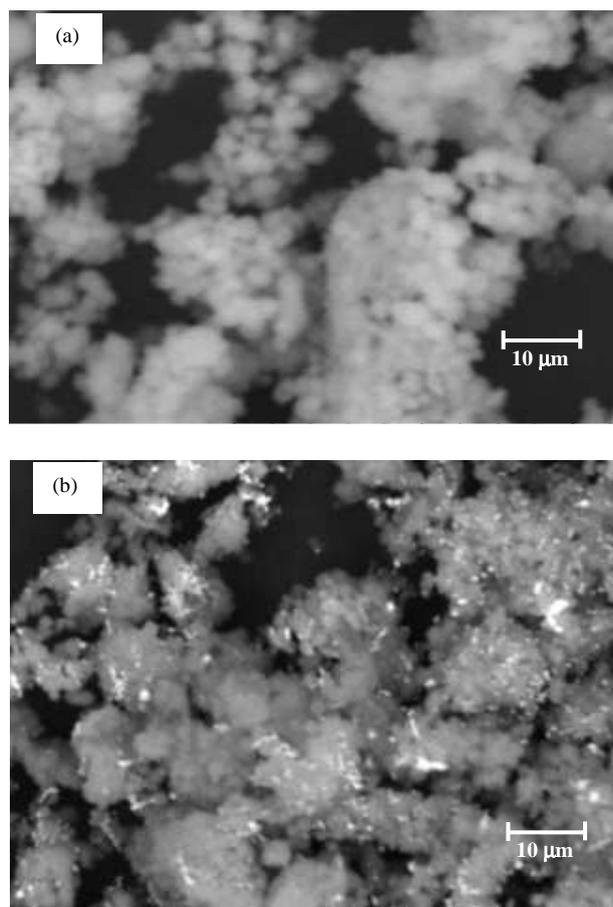


Figure 3. SEM Micrographs of (a) $\text{ZnBr}_2/\beta\text{-zeolite}$ and (b) $\text{Ni}/\text{ZnBr}_2/\beta\text{-zeolite}$

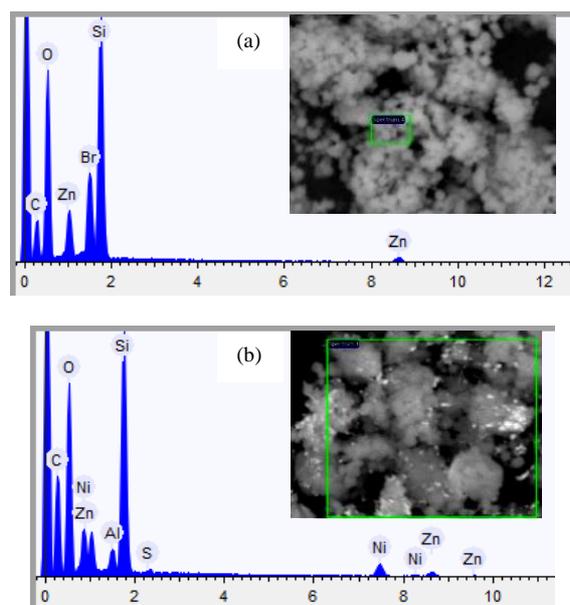


Figure 4. EDX Graphics of (a) $\text{ZnBr}_2/\beta\text{-zeolite}$ and (b) $\text{Ni}/\text{ZnBr}_2/\beta\text{-zeolite}$

The catalytic activity from $\beta\text{-zeolite}$, the $\text{ZnBr}_2/\beta\text{-zeolite}$ catalyst, and the $\text{Ni}/\text{ZnBr}_2/\beta\text{-zeolite}$ catalyst is shown in Table 1. Based on the data, the conversion of citronellal was low when using $\beta\text{-zeolite}$ as the catalyst in one-pot transformation of citronellal, but isopulegols were produced (4.19%). The conversion of citronellal was 100% when using $\text{ZnBr}_2/\beta\text{-zeolite}$ and more isopulegols were produced (64.12%). On the other hand, many products could not be identified. It is assumed that ZnBr_2 Lewis acid initiated the formation of isopulegols. Citronellal was converted rapidly over the $\text{Ni}/\text{ZnBr}_2/\beta\text{-zeolite}$ catalyst, with conversion up to 98.37% for 5 h.

Figure 5 shows the composition of product transformation of citronellal at every hour. The observed hydrogenation products after introduction to a hydrogen atmosphere for 2 h were citronellol (1.79%) and menthol (6.05%). This means that the selectivity of the catalyst toward menthol was around 6.40%. A high selectivity was not reached because the hydrogen consumption was not sufficient (we used only hydrogen atmosphere, without a hydrogen gas flow).

Table 1. Comparison of Catalytic Activities

Catalyst	Conv. (%)	Composition of Product Reactions (%)			
		1	2	3	4
a	22.89	74.02	4.19	-	-
b	100	0	64.12	-	-
c	98.36	1.57	69.68	6.05	1.78

Note:

a: $\beta\text{-Zeolite}$, b: $\text{ZnBr}_2/\beta\text{-zeolite}$, c: $\text{Ni}/\text{ZnBr}_2/\beta\text{-zeolite}$
 1: citronellal unreacted, 2: isopulegols, 3: menthols, and 4: citronellol.

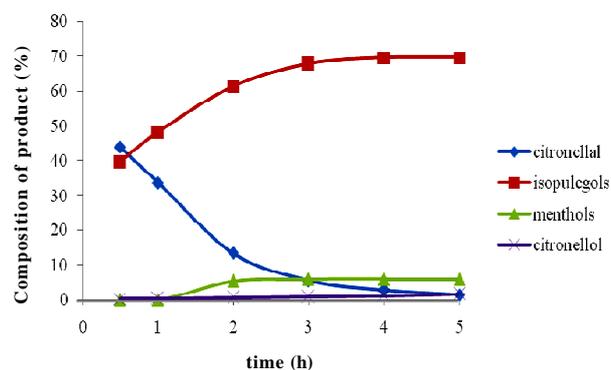


Figure 5. Composition of Product Reactions of Transformation Citronellal Over the $\text{Ni}/\text{ZnBr}_2/\beta\text{-zeolite}$ Catalyst. Reaction Conditions: 3 mL Citronellal, 0.5 g Catalyst, 120 °C, 5 h (Under a 1 atm Nitrogen Atmosphere for 1 h and Maintained Under a 1 atm Hydrogen Atmosphere for 4 h)

The results indicated that the addition of Ni on the $\text{ZnBr}_2/\beta\text{-zeolite}$ catalyst can play a role in creating cyclization sites for the formation of isopulegols and hydrogenation sites for the formation of menthols. The presence of Ni sites played the role of Lewis acid sites, which can initiate an intramolecular carbonyl-ene cyclization mechanism [9]. The plausible proposed mechanism for the cyclization of (*R*)-(+)-citronellal to isopulegols over the $\text{Ni}/\text{ZnBr}_2/\beta\text{-zeolite}$ catalyst is shown in Figure 6. Free paired electrons in oxygen atoms from the carbonyl group and electrons in π bonding interacted with unoccupied orbitals in the $\text{Ni}/\text{ZnBr}_2/\beta\text{-zeolite}$ catalyst, resulting in the intramolecular carbonyl-ene cyclization mechanism.

Based on the general mechanisms of the hydrogenation reaction for alkene using metal catalysts [20] and the catalytic reaction of citronellal [17], we identified a plausible proposed mechanism for the hydrogenation of isopulegols to menthols over the $\text{Ni}/\text{ZnBr}_2/\beta\text{-zeolite}$ catalyst, as shown in Figure 7. In the first step, electrons

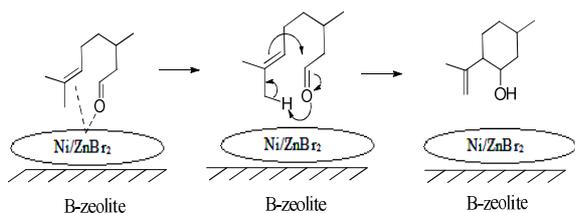


Figure 6. The Proposed Mechanism for Cyclization of (*R*)-(+)-Citronellal Over the $\text{Ni}/\text{ZnBr}_2/\beta\text{-Zeolite}$ Catalyst

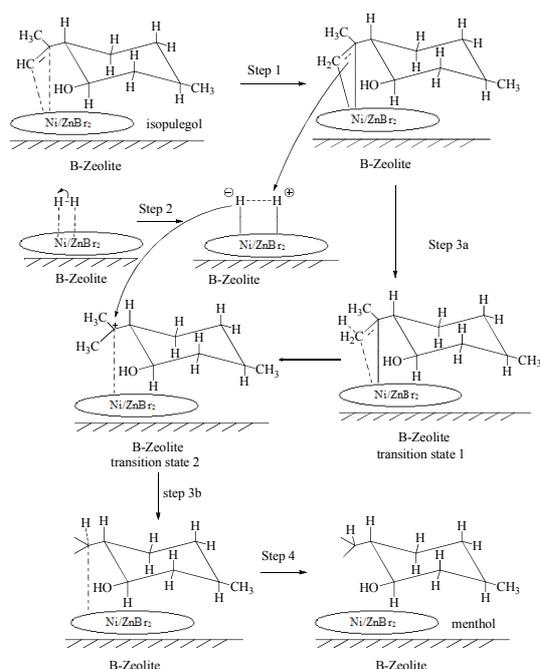


Figure 7. The Proposed Mechanism for the Hydrogenation of Isopulegols to Menthol

π on the double bond of isopulegols adsorbed on the surface of the catalyst, forming two σ bonds. Second, hydrogen molecules adsorbed on the surface of the catalyst. Third, one of hydrogen atom bonded with the C atom on alkene from the isopulegol molecule, and continued with other hydrogen atoms. Finally, hydrogenation products desorbed from the surface of the catalyst.

Despite the nickel loading on the catalyst, the rate of cyclization of isopulegols was still higher than the rate of hydrogenation of isopulegols. In addition, the presence of hydrogen in catalytic reactions can increase the rate of cyclization of (*R*)-(+)-citronellal reaction [17].

4. Conclusions

The $\text{Ni}/\text{ZnBr}_2/\beta\text{-zeolite}$ catalyst can play a role as a bifunctional catalyst for one-pot transformation of citronellal to menthols. The conversion of citronellal is 98.37%, with selectivity to isopulegol products of 73.8% and selectivity to menthol products of 6.40% over 5 h. It can be concluded that the rate of cyclization of citronellal to isopulegols is higher than the rate of hydrogenation of isopulegols to menthol.

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