Nickel Supported Natural Zeolite as a Bifunctional Catalysts for Conversion of Citronella Oil Crude to Menthols

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Abstract
Characterization and catalytic activity of modified natural zeolite for the conversion of citronella oil to menthol was investigated. In this research, natural zeolite was prepared by acid activation with HCl and impregnated with Ni metal. The addition of Ni metal of around 12.5 nm in diameter provided a bifunctional catalyst for two steps of citronella oil crude conversion i.e. cyclization and hydrogenation. The process was performed in a one-pot reaction system by stirring at 200°C with pressure of 20 bar H2 for 3h. The reaction products changed slightly with varieties of reaction temperature and amount of catalysts employed. Results showed that Ni/NZB-HT catalyst was the best catalyst which was able to convert citronella oil to menthol with a selectivity of 50% menthol and 100% conversion of citronellal.

Keywords: Natural Zeolite, Nickel Catalyst, Citronella Oil, Menthol

1. INTRODUCTION

Citronella oil is the main product of Java citronella grass (Cymbopogon winterianus Jowitt) widely used in cosmetics, fuel additives and pharmaceuticals industries. It has three main components; citronellol, citronellol, and geraniol. Indonesia as one of the world’s largest producers of citronella oil has produced approximately 350 tons of citronella oil annually [1]. The derivatives of citronella oil can provide high value added chemicals for many industries such as menthol. Synthesis of menthol from citronellal can be performed through a two-step reaction, first, cyclization of citronellal to isopulegol over an acid catalyst, and the second, hydrogenation process to menthol over a metal catalyst.

Zeolite is a crystalline solid structure composed by tetrahedral alumina (AlO45−) and silicate (SiO44−). Zeolite can be divided into two types, natural zeolite which contains several cations such as K+, Na+, Ca2+ or Mg2+ and synthetic zeolite which mainly only contains K+ or Na+ cations [2]. Brönsted acid sites are formed and may modify zeolites into solid acid catalysts. Indonesia has an abundant natural zeolite source spread out in Java, NTT, Papua, Sumatra, Sulawesi, and Borneo. The highest deposit of zeolite was recorded up to 400 million tons in West Java with mordenite and clinoptilolite as the common types in this area.

Ni/ZnBr/β-zeolite can transform citronellal to isopulegol and menthol in a one pot reaction system, with a selectivity to isopulegol of 73.8% and menthol of 6.40% [3]. The presence of Ni sites played the role of Lewis acid sites, which can initiate an intermolecular carbonyl and cyclization mechanism. Adilina, et al. (2015) used nickel supported natural zeolites (Ni/NZ) as catalysts in a two stage reaction of citronellal to menthols. Preparation of catalyst using an ion exchange method was able to convert citronellal derivatives to 9% menthol with 36% selectivity [4].

In this study, natural zeolite was designed as catalysts for the green conversion of citronella oil to menthol. These catalysts was prepared through modification of natural zeolite with Ni
metal, and therefore it was expected to have bifunctional catalytic properties; acid site (metal oxide in natural zeolite) and hydrogenation site (Ni metal), which are required for conversion of citronella oil derivatives compounds. Immobilization of Ni metal will be performed by impregnation method and various reaction parameters will be studied. With this study, local natural zeolites may participate in green technology which provides a significant role in national development, both as a prime export commodity mining and raw material in the domestic industries. In addition, the synthesis of menthol provides a product of high value from Indonesia citronella oil.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation and Characterization

Natural zeolite used in this experiment was taken from Bogor, Indonesia. This zeolite with the sizes of 200 mesh contain SiO$_2$ higher than Al$_2$O$_3$ as previously reported [4]. Acidified Natural Zeolite (NZB) was prepared through acid activation using HCl 1 M and stirring for 1 h. The solution was filtrated and rinsed with distilled water until the solution was neutral (pH: 6-7). The activated zeolite was then dried at 250°C for 3 h and used as catalyst support.

Nickel supported natural zeolite (Ni/NZB) was prepared by impregnation method at 80°C with ethanol solutions containing 20 wt% Ni from Ni(NO$_3$)$_2$·6H$_2$O salt. The solution was stirred until the solvent was slowly removed. After the impregnation, the resulting Ni/NZB was dried at 120°C for 2 h. Calcination was conducted at 500°C for 2 h. The specific surface area, pore size distribution, and pore volume of samples were estimated by the Barret-Joyner-Halenda (BJH) method using N$_2$ adsorption-desorption curves (Micromeritic TriStar II, Flow Prep 060). Crystallization behaviors of the samples were investigated with X-ray diffractometer (Rigaku Smart Lab 3KW X-Ray Diffractometer, Cu Kα Radiation). Alteration in the microstructure of samples during heating were discussed using Thermogravimetric Analysis and Differential Scanning Calorimetric TG-DSC (Linseis STA PT 1600), and the grain sizes of the samples were estimated from the images observed by TEM (FEI type Tecnai G2 20S-Twin).

2.2. Catalytic Activity

The conversion of citronella oil was carried out in a 200 mL autoclave by heating 6.5 mmol citronella oil and Ni/NZB catalysts at 200°C for 3 h by stirring at a pressure of 20 bar H$_2$. The amount of catalyst was varied between 5 wt% and 10 wt% of reactant. The products were analyzed by GC-Mass Spectrometry (Agilent 19091S, column HP-5MS (30 m x 250 m, 0.25 m)).

3. RESULT AND DISCUSSION

3.1. Preparation and Characterization of Catalysts

The presence of elements such as K$^+$, Na$^+$, Ca$^{2+}$ or Mg$^{2+}$ in the zeolite surface can affect activity of zeolite used in the reaction (Table 1). Pretreatment, such as milling, heating and acid treatment, is necessary to improve the character of natural zeolite. In this research, activation of natural zeolite performed by an ion exchange method using HCl 1 M at room temperature for 1 hour replacing several ions such as K$^+$, Na$^+$, Ca$^{2+}$ or Mg$^{2+}$ with H$^+$ (Lewis acid site) which is required in the cyclization reaction of citronellal. Yilmaz, et al. (2005) reported that the presence of Fe as an impurity and the electrostatic field produced by the constituent ions (e.g., Na, K) being part of the zeolite structure was reported to improve the selectivity to unsaturated alcohols (citronellol) [5].

Table 1. Chemical composition of natural zeolite (NZB)

| Component | %     |
|-----------|-------|
| SiO$_2$   | 72.27 |
| Al$_2$O$_3$| 14.74 |
| K$_2$O    | 5.30  |
| CaO       | 3.41  |
| Fe$_2$O$_3$| 2.41  |
| Others    | 1.87  |
In addition, activation of zeolite will dissolve inorganic ions on the surface of the natural zeolite. The increase of surface area of zeolite was observed after acid treatment using HCl (Table 2). The average pore diameter of zeolites in the range of >2 nm indicates that the natural zeolite is dominated with mesoporous (2 ~ 50 nm, IUPAC).

Table 2. Specific surface area, pore volume, and pore size distribution of samples

| Samples     | Surface Area (m² g⁻¹) | Pore Volume (cm³ g⁻¹) | Average Pore Diameter (nm) |
|-------------|-----------------------|-----------------------|----------------------------|
| NZB         | 16                    | 0.004                 | 2.11                       |
| NZB-actived | 78                    | 0.006                 | 2.07                       |
| Ni/NZB      | 17                    | 0.003                 | 2.08                       |
| Ni/NZB-CL   | 29                    | 0.004                 | 2.08                       |
| Ni/NZB-CLHT | 29                    | 0.003                 | 2.08                       |
| Ni/NZB-HT   | 37                    | 0.005                 | 2.08                       |

Note: CL: calcination, CLHT: calcination-reduction, HT: reduction

The immobilization of Ni metal in natural zeolites have been reported by using an impregnation method. Ni is inexpensive and widely known for good activity in hydrogenation reactions. However, the active sites of the zeolite does not have a large surface area. The reaction becomes ineffective and inefficient because all active centers are not able to contact with the reactants. Therefore, the Ni metal is required to be distributed on a solid support with a large surface area like zeolite [6]. In this study, Ni/NZB catalysts were synthesized using 20 wt% of Ni metal. Ni was expected to increase the activity of the catalyst in the hydrogenation of citronellal reaction. We also observed the differences in characteristics and activity of the catalysts which was synthesized through calcination and hydrogen treatment (CLHT) processes compared with direct hydrogenation process on catalyst without calcination (HT).

The specific surface area, pore volume, and pore size distribution of samples were estimated by the Barret-Joyner-Halenda (BJH) method using N₂ adsorption-desorption curves. Table 2 shows the comparison of NZB before and after activation using HCL, and Ni/NZB catalysts. The surface area of the Ni/NZB catalysts decreased compared to the activated NZB. This is possible because the Ni metal was entrusted to the buffer and covered the surface of the zeolite pores. After calcination, the surface area of zeolite increased. The calcination stage used a relatively high temperature hence the distribution of Ni on the surface of the pores was evenly distributed to form the oxide. Other compounds such as NO₂, O₂, H₂ which were trapped in the pores of the catalyst were able to be released in this phase. The surface area of Ni/NZB-HT was observed to be the highest.

The XRD pattern of NZB and Ni/NZB catalysts were given in Figure 1(a). Characteristic peaks of mordenite (2θ = 9.84°, 13.48°, 22.34°, 25.74°, 26.66°, 27.68°) phases were detected in the NZB structure. A high peak intensity at 2θ = 26.66° indicated that mordenite was the main constituent mineral, although a few clinoptilolite peaks (2θ = 11.2°, 19.72°, 22.42°, 25.82°, 27.92°) was observed. When compared to the Ni/NZB catalysts, there was no change in the value of 2θ. After the immobilization with Ni, the intensity of these peaks increased. Therefore, it can be assumed that the calcination process was able to remove impurities in the framework of zeolite.
Fig. 1. (a) Diffractograms of catalyst samples, (b) TEM image of the Ni/NZB-HT catalyst.

Figures 1(b) shows the TEM image of the Ni/NZB catalyst. The Ni particles were well dispersed over the NZB support, confirmed by the observation of black dots with small grains, around 12.5 nm in diameter. These particles should be exclusively localized on the outer surface of the zeolite crystallites.

Results of TG/DSC profile is shown in Figure 2. A weight lost of the catalyst at a temperature of 80°C accompanied by endothermic peak may be attributed to evaporation of water on the catalyst. Meanwhile, an exothermic peak at around 580°C and a weight loss of 14% indicated that the evaporation of crystal water and combustion of residual organic compounds in the zeolite structure. The water content in the catalyst was also calculated based on the changes in mass at temperatures between 30 °C-120 °C, which was up to 7%. The increase in mass of the catalyst shown at the temperature >580°C, indicated that oxidation reaction occurs in the Ni metal with oxygen from the air to form NiO compound [7]. According to the results, the temperature of calcination was reached at 500°C. Extending the heating time over 2 h can eliminate the organic compounds contained in pore of the catalyst.

3.2. Conversion of citronella oil to menthol

The cyclization-hydrogenation reactions of citronella oil in a one-pot reaction system was carried out in an autoclave by heating at 200°C temperature for 3 hours with 20 bar of H₂ pressure. Citronella oil used in the reactions was the result of fractionation distillation of citronella oil with >60% citronellal content as well as other components such as linalool and citronellol. Isopulegol is an intermediate compound of the cyclization of citronellal in the presence of an acid catalyst (Scheme 1).

Scheme 1. (i) cyclization of citronellal to isopulegol, (ii) hydrogenation of isoeugenol to menthol.

The C=C and C=O bond of citronellal was destabilized due to the high acidity of the catalyst where an interaction between electrons on the carbonyl and π electrons on the C=C bond with the Lewis acid site catalyst occurred and accompanied by protonation of the Brönsted acid to form isopulegol. According to Chuah et al. (2001), the catalyst having a weak Brönsted acid site and higher Lewis acid site will have a high selectivity in cyclization reaction of citronellal.
Almost all the catalytic activity of the Ni/NZB catalysts in this study resulted the isopulegol compound with yield of >4% (Table 3). Catalysts Ni/NZB-CLHT-5 with amount of 5wt % catalyst was able to selectively form isopulegol up to 50% (50% selectivity). The lowest yield of isopulegol was achieved by using Ni/NZB-HT-10 catalyst, however, a higher yield of menthol was observed. This is possible due to most of the isopulegol compounds are hydrogenated into menthols.

Citronellal has two active functional groups which is attached to the carbonyl C atom and double bond (C=C). The existence of carbonyl (C=O) in citronellal allow hydrogenation reactions to form compounds that produce citronellol alcohol group (C-OH). A highly acidic catalyst may directly yield products of hydrogenated citronellal, citronellol and 3,7-dimethyl-1-octanol, as a result of their interaction with the metal Ni π bond.

Conversion of citronellal oil was performed using two different amount of catalyst to reactants, i.e. 5 wt% and 10 wt%. Product analysis by GC-MS is shown in Table 3. From these results, it was observed that the Ni/NZB-HT-10 catalyst with 10 wt% amount of catalyst was able to produce menthol compounds up to 50% selectivity. On the other hand, the yield of menthol (12%) was lower using Ni/NZB-HT-5 catalyst. This is probably due to the lack of Ni metal active site in Ni/NZB-HT-5 compared to Ni/NZB-HT-10 which plays an important role in the hydrogenation of isopulegol to menthol.

The effect of temperature was performed at 100°C, 200°C, and 300°C. The product distributions slightly changed with the increase of temperature for a given conversion. In the beginning, citronellal was converted to 50% isopulegol but no menthol was formed. This was due to the formation of undesirable products of catalytic cracking of isopulegol at high temperatures. The cyclic structure of isopulegol seems to easily decompose in higher reaction temperatures yielding byproducts other than the desired menthol.

Table 3. GC-MS Analysis result for Conversion of Citronella Oil to Menthols.

| Catalyst          | Conversion (%) | Yield Citronelol (%) | Yield Isopulegol (%) | Yield Menthol (%) | Yield Others (%) | Selectivity of Menthol (%) |
|-------------------|----------------|----------------------|----------------------|-------------------|-----------------|--------------------------|
| NZB-5             | 100            | 0                    | 12                   | 0                 | 88              | 0                        |
| NZB-10            | 100            | 0                    | 10                   | 0                 | 90              | 0                        |
| Ni/NZB-HT-5       | 100            | 4                    | 41                   | 12                | 43              | 12                       |
| Ni/NZB-HT-10      | 100            | 5                    | 10                   | 50                | 35              | 50                       |
| Ni/NZB-CLHT-5     | 100            | 1                    | 50                   | 0                 | 49              | 0                        |
| Ni/NZB-CLHT-10    | 100            | 1                    | 18                   | 18                | 63              | 18                       |
| Ni/NZB-HT-10\(^a\) | 51             | 0                    | 5                    | 0                 | 46              | 0                        |
| Ni/NZB-HT-10\(^b\) | 100           | 5                    | 4                    | 14                | 77              | 14                       |

Reaction conditions: 1 gr citronella oil, 200°C, 3 hours, 20 Bar, CLHT: calcination-reduction; HT : reduction, Amount of catalysts 5: 5 wt%, 10: 10 wt%, Variety of temperature: \(^a\) 100°C, \(^b\) 300°C.
4. CONCLUSION

The nickel supported on zeolite catalysts played a role as a bifunctional catalyst for the one-pot transformation of citronellal to menthols at 200 °C with pressure of 20 bar H₂ for 3h. These catalysts were prepared from natural zeolite by acid activation and immobilization of Ni metal using an impregnation method. High activity and selectivity for 50% isopulegol was reached using the Ni/NZB-CLHT catalyst which was synthesized by a calcination-hydrogen treatment process. Meanwhile Ni/NZB-HT catalyst which was synthesized by direct hydrogenation treatment showed the highest activity and selectivity for menthol ranging up to 50%. A lower catalytic activity giving only 51% conversion of citronellal was seen using the Ni/NZB-HT catalyst when the reaction temperature was lowered to 100 °C. On the other hand, increasing the temperature to 300 °C gave high conversion of 100% but mainly resulted undesirable catalytic cracking products. These nickel supported on zeolite catalysts are therefore promising materials for the conversion of citronella oil to value added flavor chemicals especially menthols.

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