CONVERSION OF CITRONELLA OIL AND ITS DERIVATIVES TO MENTHOL OVER BIFUNCTIONAL NICKEL ZEOLITE CATALYSTS

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Abstract
Citronella oil and its derivatives were converted to menthol in a one-pot reaction system using bifunctional zeolite based nickel catalysts. The catalysts were prepared by immobilization of nickel on natural zeolite (NZ) and synthetic zeolite (ZSM-5) by a simple cation exchange method. Catalytic reactions were carried out at 70 °C by first stirring the mixture in air for cyclization of citronellal to isopulegol followed by hydrogenation of isopulegol to menthol at 2 MPa of H₂ pressure. The Ni/NZ catalyst was able to convert 24% of a citronella oil derivative yielding 9% menthol (37% selectivity), whereas Ni/ZSM5 catalyst showed lower activity of with 65% conversion and 4% yield of menthol (6% selectivity). These zeolite based catalysts are therefore potential materials for the conversion of biomass feedstock to value-added fine chemicals.

Keywords: bifunctional catalyst, zeolite, nickel, citronella oil, menthol

I. INTRODUCTION
Citronella oil is considered one of the 20 most important essential oils that are traded worldwide [1] and widely used in the manufacture of perfume, soap, and many other cosmetics. This essential oil is categorized into two types in the global market; Ceylon citronella oil which is provided from the Cymbopogon nardus grass plant and Java type citronella oil obtained from that of Cymbopogon winterianus [2]. Indonesia is the third largest world producer of citronella oil (after China and Vietnam) with estimated production of 350 tons annually [3]. The major components in citronella oil include citronellal, citronellol, and geraniol.

Menthol is a flavor chemical which is used extensively in food, cosmetic, and pharmaceutical industries [4]. Natural menthol can be supplied through extraction of Mentha arvensis plant followed by a separation process. Meanwhile synthetic (-)menthol is industrially produced by Takasago International Corp. and Symrise using myrcene or m-cresol as the protocol in a catalytic process involving consecutive steps. Synthesis of menthol from citronellal, on the other hand, may be performed by a more effective two step process, i.e. one-pot cyclisation of citronellal followed by hydrogenation of isopulegol to menthol [5].

Acid catalysts such as SiO₂, Al-MCM-41, ZnBr₂, has reported to serve as an efficient cyclization catalyst of citronellal. The Brønsted acid site was able to increase the rate of isomerization of citronellal although the formation of (-) isopulegol was still low. Zinc bromide, which gives 94% selectivity to isopulegol, is used industrially.

The hydrogenation reaction of isopulegol to menthol requires metal catalysts which can accelerate the reaction rate. Ni metal exhibits high activity in the processes of cracking, isomerization, hydrogenation, as well as ring opening of hydrocarbons and a Ni/Al-MCM-41 catalyst was reported to transform citronellal to menthol in good selectivity [4]. The weak acid sites of Al-MCM-41 facilitated the cyclisation of citronellal to isopulegol, and upon hydrogenation 70–75% racemic (±)-menthol was formed. Various studies have reported the use of Ni metal as an active metal on catalyst for the hydrogenation reaction of isopulegol to menthol, including Ni/ ZnBr₂β-zeolite catalyst [6], NiZrS catalyst [7], and Ni/γ-Al₂O₃ catalyst [8].

In this paper, we present the preparation of bifunctional nickel zeolite catalysts from natural zeolite (NZ) and synthetic zeolite (ZSM-5) and their application in the one-pot synthesis of menthol from citronella oil and its derivatives. NZ based catalysts are considered more economical than other synthesized silica-alumina compounds since these materials are abundant and readily available whereas ZSM-5 is commercially available and was used for comparison. Ni metal was chosen due to its low cost compared to precious metals such as Pt, Pd, and Ru.
II. EXPERIMENTAL
A. Preparation and Characterization of Bifunctional Zeolite Based Catalysts
Nickel supported on zeolite (NZ, ZSM5) was prepared via an ion exchange procedure by adding 5 g zeolite to an amount of distilled water containing 10 wt% Ni from Ni(NO$_3$)$_2$.6H$_2$O (Merck). The solution was stirred at room temperature for 24 h. The catalyst was then dried at 100 ºC for 2 h and then calcined at 350 ºC for 2 h. Before the catalytic testing, some catalysts were reduced under H$_2$ flow for 2 h at 300 ºC and 500 ºC for NZ and ZSM5 catalysts, respectively. Characterization of the catalysts was conducted by a surface area analyser, X-ray fluorescence, and X-ray diffraction.

B. Catalytic Test and Product Analysis
The catalytic test was carried out in a 20 mL autoclave at 70 ºC. Citronella oil and its derivatives (5 mmol) was added into the autoclave and 0.1 g bifunctional catalyst was added with 5 mL cyclohexane (Merck). After 3 h, H$_2$ was flowed with a constant pressure of 2 MPa for another 3 h. Reaction products were analyzed by gas chromatography using biphenyl as an internal standard (Shimadzu 14A, column DB5-MS 30 m x 0.25 m x 0.25 μm, FID detector).

III. RESULT AND DISCUSSION
A. Characterization of Bifunctional Zeolite Based Catalysts
1) Surface area analyzer measurement
The surface area, pore size, volume, and pore size of the various bifunctional zeolite based catalyst were measured by a surface area analyzer according to the BET method. As can be observed in Table 1, the surface area of Ni/NZ (entry 2) and Ni/NZ-HT (entry 3) increased slightly after immobilization and subsequent hydrogen treatment, respectively. Meanwhile natural zeolite as the catalyst precursor tends to show a smaller surface area and pore volume (entry 1). This is presumably due to a number of impurities in their framework which may cover the active surface. In the case of Ni/ZSM5 and Ni/ZSM5-HT, the surface area was detected lower than that of the parent ZSM-5, although the change of their pore volume and pore size was neglectable. It is predicted that a partial blockage of porous structure in the ZSM-5 framework occurred after the Ni loading.

Table 1.
Surface area, pore volume, and pore size of Ni/NZ and Ni/ZSM5 catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NZ</td>
<td>16</td>
<td>0.004</td>
<td>2.11</td>
</tr>
<tr>
<td>2</td>
<td>Ni/NZ</td>
<td>26</td>
<td>0.01</td>
<td>2.10</td>
</tr>
<tr>
<td>3</td>
<td>Ni/NZ-HT$^a$</td>
<td>35</td>
<td>0.01</td>
<td>2.10</td>
</tr>
<tr>
<td>4</td>
<td>ZSM-5$^{b)}$</td>
<td>400</td>
<td>0.03</td>
<td>2.03</td>
</tr>
<tr>
<td>5</td>
<td>Ni/ZSM5</td>
<td>361</td>
<td>0.03</td>
<td>2.03</td>
</tr>
<tr>
<td>6</td>
<td>Ni/ZSM5-HT$^a$</td>
<td>342</td>
<td>0.03</td>
<td>2.04</td>
</tr>
</tbody>
</table>

$^a$HT : Hydrogen treatment

2) X-ray fluorescence analysis
Table 2 summarizes the elemental composition of SiO$_2$ and Al$_2$O$_3$ in the Ni/NZ and Ni/NZ-HT catalysts. Results show that both catalysts have a SiO$_2$ content higher than that of AlO$_3$. The Si/Al ratio is the ratio of the number Si atoms to the number of Al atoms in the zeolite framework and a higher Si/Al ratio is known to give a higher acid behavior [10]. The Ni content was measured as 1% for both Ni/NZ and Ni/NZ-HT catalysts.

Table 2.
Elemental Analysis of NZ Based Catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>SiO$_2$ (%)</th>
<th>Al$_2$O$_3$ (%)</th>
<th>NiO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NZ</td>
<td>72</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Ni/NZ</td>
<td>72</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Ni/NZ-HT</td>
<td>71</td>
<td>15</td>
<td>1</td>
</tr>
</tbody>
</table>
3) X-ray diffraction analysis

The crystalline structure of a number of Ni/NZ catalysts were determined by XRD analysis. XRD patterns of the parent NZ and that after immobilization of Ni are shown in Fig. 2. According to the results, clinoptilolite (2θ = 13.68°, 26.78°, 30.12°) and mordenite (2θ = 19.74°, 22.42°, 25.82°, 27.92°) phases were detected in the NZ structure. A high peak intensity at 2θ = 26.78° indicates that the parent NZ compose of moderite as its main constituent mineral with some existence of clinoptilolite.

Meanwhile when compared with the Ni/NZ catalyst, no change in the value of 2θ from was observed, however, the peaks intensity increased after the immobilization. This is suggested due to the calcination process which may remove impurities in the NZ framework. In the case of
Ni/NZ-HT catalyst, a new peak at $2\theta = 41.74^\circ$ was formed, indicating that the presence of Ni metal in the structure as a result of hydrogenation treatment.

B. Conversion of Citronellal and Its Derivatives to Menthol

Conversion of citronellal and its derivatives to menthol over various bifunctional Ni zeolite based catalysts was carried out in an autoclave at 70°C such as summarized in Table 4. The catalytic activity was first tested for Ni/ZN catalyst for 24 h using cyclohexane as a solvent and 100% conversion of citronellal was obtained. The catalyst was able to yield 7% of isopulegol, the intermediate of menthol, however, no formation of menthol was observed (entry 1). Other byproducts are predicted to be citronellol, 3,7-dimethyloctanal, and 3,7-dimethyloctenal. When toluene was used as the solvent, no significant increase in the isopulegol and menthol yield was seen (entry 2). It has been reported that catalysts with weak Brønsted acid and high Lewis acid sites will give a high selectivity in the cyclization reaction of citronellal to isopulegol [11].

To determine whether the Ni metal active site in the catalyst was effective for the hydrogenation reaction, catalytic reactions using citronellal and isopulegol as the starting material were conducted using Ni/NZ-HT catalyst. Results reveal than no yield of menthol was obtained when citronellal was used as the reactant (entry 3). On the other hand, 8% yield of menthol could be obtained from isopulegol with 24% conversion giving 37% selectivity (entry 4). From these results, it can be observed that the Ni/NZ catalyst was indeed able to act as a bifunctional catalyst for the conversion, although the Ni metal active site cannot play its role more efficiently in the hydrogenation reaction since the number of isopulegol formed from citronellal is still low. In the cases of Ni/ZSM5 and Ni/ZSM%-HT catalysts, lower conversions citronellal were seen and only 4% menthol was formed. Nevertheless, higher yields of 21% isopulegol were obtained (entry 5-7). Finally, control reaction without the use of any catalysts did not give any conversion of citronellal (entry 8) which shows that the presence of catalysts is highly essential for the conversion of citronella oil and its derivatives to menthol.

IV. CONCLUSION

Bifunctional Ni zeolite catalysts were successfully prepared from natural zeolite (NZ) and synthetic zeolite ZSM-5 (ZSM-5) by immobilization of Ni using a cation-exchange procedure. Their catalytic activity were tested in the one-pot synthesis of menthol from citronella oil and its derivatives. Ni/NZ-HT showed the highest catalytic of 24% conversion yielding 8% of menthol and 6% selectivity whereas a lower catalytic activity of 64% conversion and 4% yield of menthol was seen for the Ni/ZSM5 catalyst. Therefore, both Ni zeolite catalysts are potential materials for the synthesis of flavor chemicals from citronella oil.

Table 4.
Conversion of citronellal and its derivatives to menthol using various catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Yield isopulegol (%)</th>
<th>Yield menthol (%)</th>
<th>Yield others (%)</th>
<th>Selectivity menthol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Ni/NZ</td>
<td>10</td>
<td>7</td>
<td>0</td>
<td>93</td>
<td>0</td>
</tr>
<tr>
<td>2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Ni/NZ</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>86</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Ni/NZ-HT</td>
<td>97</td>
<td>12</td>
<td>4</td>
<td>0</td>
<td>85</td>
</tr>
<tr>
<td>4&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Ni/NZ-HT</td>
<td>24</td>
<td>8</td>
<td>12</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>5&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Ni/ZSM5</td>
<td>64</td>
<td>21</td>
<td>4</td>
<td>0</td>
<td>43</td>
</tr>
<tr>
<td>6</td>
<td>Ni/ZSM5-HT</td>
<td>48</td>
<td>8</td>
<td>14</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>7&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Ni/ZSM5-HT</td>
<td>77</td>
<td>14</td>
<td>2</td>
<td>0</td>
<td>61</td>
</tr>
<tr>
<td>8</td>
<td>Blank</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Reaction conditions: citronellal (5 mmol), catalyst (0.1 g), cyclohexane (5 mL), 70 °C, 6h, 2 MPa H₂.
<sup>a</sup> reaction time: 24 h, <sup>b</sup> toluene as solvent, <sup>c</sup> isopulegol as reactant, <sup>d</sup> catalyst: 0.2 g.
References


