

CONVERSION OF (\pm)-CITRONELLAL AND ITS DERIVATIVES TO (-)-MENTHOL USING BIFUNCTIONAL NICKEL ZEOLITE CATALYSTS

(Konversi (\pm)-Citronellal dan Turunannya Menjadi (-)-Mentol Menggunakan Katalis Nikel Zeolit Dwi-Fungsi)

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ABSTRAK. (\pm)-Citronellal and its derivatives were converted to (-)-menthol by a one-pot reaction system using zeolite based nickel catalysts. The catalysts were prepared by immobilization of nickel on natural zeolite (NZ) or synthetic zeolite (ZSM-5) by a simple cation exchange method. Calcination and hydrogen treatment procedures were able to significantly increase the surface area and pore volume of NZ based catalysts whereas negligible changes in the properties were observed for that of ZSM-5. Catalytic reactions were carried out at 70°C by stirring the mixture in the air for cyclization of (\pm)-citronellal to (\pm)-isopulegol followed by hydrogenation towards the desired (-)-menthol at 2 Mpa of H₂ pressure. The Ni/NZ catalyst was able to convert a (\pm)-citronellal derivative yielding 9% (-)-menthol (36% selectivity) with conversion up to 24%, whereas Ni/ZSM5 catalyst directly converted 65% (\pm)-citronellal to give 4% menthol (6% selectivity). These zeolite based catalysts are therefore potential materials for the conversion of biomass feed stock to value-added chemicals.

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

ABSTRACT. (\pm)-Sitronelal dan turunannya telah dikonversi menjadi (-)-mentol dalam sistem reaksi one-pot menggunakan katalis nikel berbasis zeolit. Katalis dipreparasi melalui imobilisasi nikel pada zeolit alam (NZ) atau zeolit sintetik (ZSM-5) dengan metode pertukaran ion. Prosedur kalsinasi dan perlakuan hidrogen dapat meningkatkan secara signifikan luas permukaan dan volume pori dari katalis berbasis NZ sedangkan perubahan yang tidak besar terlihat untuk ZSM-5. Reaksi katalitik dilakukan pada suhu 70°C dengan mengaduk campuran di dalam udara untuk siklisasi (\pm)-sitronelal menjadi (\pm)-isopulegol dilanjutkan dengan hidrogenasi menjadi (-)-mentol pada 2 Mpa tekanan H₂. Katalis Ni/NZ dapat mengkonversi turunan (\pm)-sitronelal menghasilkan 9% mentol (selektifitas 36%) dengan konversi sampai 24%, sedangkan katalis Ni/ZSM5 mengkonversi 65% (\pm)-sitronelal dan menghasilkan (-)-mentol 4% (selektifitas 6%). Katalis berbasis zeolit ini adalah material yang berpotensi untuk konversi bahan biomasa menjadi bahan kimia bernilai tambah.

Kata kunci: katalis nikel, mentol, minyak sereh wangi, sitronelal, zeolit

1. INTRODUCTION

Menthol is a flavor chemical, which is used extensively in food, cosmetic and pharmaceutical industries (Nie, *et.al.*, 2007). 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, however, the process involves consecutive steps and require an amount of homogeneous catalysts to aid the reaction. The developments of

alternative methods are strongly desired, especially those using a more effective protocol which can minimize synthetic steps together with a more environmentally friendly heterogeneous catalyst.

Synthesis of (-)-menthol from citronellal, may be performed in a one-pot reaction system by an effective two step process, i.e. cyclisation of (+)-citronellal to (-)-isopulegol followed by hydrogenation of the isopulegol to (-)-menthol (Mertens, *et.al.*, 2003). Acid catalysts such as SiO_2 , Al-MCM-41 and ZnBr_2 , have been reported to serve as an efficient cyclization catalyst of citronellal. The Bronsted acid site was able to increase the rate of citronellal isomerization although formation of (-)-isopulegol were still low. Industrially, ZnBr_2 is used and may give 94% selectivity to isopulegol, however, the process implies the use of some compounds harmful to the environment.

For the second process, the hydrogenation reaction of isopulegol to menthol requires a metal catalyst which can adsorb hydrogen molecules and accelerate the reaction. Ni is a low cost base metal which exhibits high activity in the processes of cracking, isomerization, hydrogenation, as well as ring opening of hydrocarbons. 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/ ZnBr_2 / β -zeolite catalyst (Nisyak, *et.al.*, 2013), NiZrS catalyst (Cortes, *et.al.*, 2011) and Ni/ γ - Al_2O_3 catalyst (Iftitah, *et.al.*, 2011). A Ni/Al-MCM-41 catalyst was reported to transform citronellal to menthol in good selectivity (Nie, *et.al.*, 2007). The weak acid sites of Al-MCM-41 facilitated the cyclisation of citronellal to isopulegol and upon hydrogenation, 70–75% racemic (\pm)-menthol was formed.

Zeolite is an aluminosilicate mineral and may exhibit both Bronsted and Lewis acid sites which are essential for the conversion of citronellal to menthol. Pt/H-beta zeolite was reported to assist the one-step formation giving 76% yield of (-)-menthol (Mertens, *et.al.*, 2006). Nevertheless, the use of non-expensive Ni

metal is more favourable than precious metals such as Pt, Pd and Ru. We have previously reported the conversion of citronellal to isopulegol using acidified natural zeolite H-NZ, natural bentonite H-NB, and synthetic zeolite H-ZSM5 catalysts (Adilina, *et.al.*, 2014). A higher selectivity of 86% isopulegol was obtained using H-NZ compared to that of H-NB and H-ZSM5 in mild reaction conditions. Further application of H-NZ was evaluated for the one-pot synthesis of menthol from citronellal using dual-catalyst system of the acidified natural zeolite and Raney-Ni catalyst, conversion of (\pm)-citronellal up to 80% was achieved giving 68% (v/v) formation of racemic (\pm)-menthol (Adilina, *et.al.*, 2008). Besides the fact that NZ based catalysts are considered more economical than other synthesized silica-alumina compounds since these materials are abundant and readily available, modification through immobilization of metals of the zeolite creates extra Lewis acidity on the catalyst and results in a higher selectivity for the desired menthol. 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 (\pm)-citronellal and its derivatives.

2. RESEARCH METHODS

Preparation and Characterization of Zeolite Based Catalysts

Nickel supported on zeolite (NZ, ZSM5) was prepared via typical cation exchange procedure (Kimball, *et.al.*, 1981) by adding 5 g zeolite to an amount of distilled water containing 10 wt% Ni from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck). The solution was stirred at room temperature for 24 h. The catalyst was then dried at 100°C for 2 h and then calcined at 350°C for 2 h. Before the catalytic testing, some catalysts were reduced under H_2 flow for 2 h at 300°C and 500°C for NZ and ZSM5 catalysts, respectively. Characterizations of the catalysts were conducted by a surface area analyser, X-ray fluorescence and X-ray diffraction.

Catalytic Testing and Product Analysis

The catalytic test was carried out in 20 mL autoclave at 70°C as previously reported by Adilina, *et.al.* (2008). (\pm)-Citronellal 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, H₂ 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 μ m, FID detector).

3. RESULTS AND DISCUSSION

Characterization of Bifunctional Zeolite Based Catalysts

1) Surface area analyzer measurement

The surface area, pore size, volume, and pore size of 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.

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

Entry	Catalyst	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore Size (nm)
1	NZ	16	0.004	2.11
2	Ni/NZ	26	0.010	2.10
3	Ni/NZ-HT ^a	35	0.010	2.10
4	ZSM-5 ^b	400	0.030	2.03
5	Ni/ZSM5	361	0.030	2.03
6	Ni/ZSM5-HT ^a	342	0.030	2.04

^aHT : Hydrogen treatment

^bBased on experimental data obtained by Lawrence (1993)

Meanwhile natural zeolite as the catalyst pre cursor tends to show a smaller surface area and pore volume (entry 1). This is presumably due to a number of impurities in their framework such as oxides of Na, K, Ca, Mg and Fe, 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.

2) X-ray fluorescence analysis

Table 2 summarizes the elemental composition of SiO₂ and Al₂O₃ in the Ni/NZ and Ni/NZ-HT catalysts. Results show that both catalysts have SiO₂ content higher than that of Al₂O₃. 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. The Ni content was measured as 1% for both Ni/NZ and Ni/NZ-HT catalysts.

Table 2. Elemental Analysis of NZ Based Catalysts

Entry	Catalyst	SiO ₂ (%)	Al ₂ O ₃ (%)	NiO (%)
1	NZ	72	15	-
2	Ni/NZ	72	14	1
3	Ni/NZ-HT	71	15	1

3) X-ray diffraction analysis

The crystalline structures of Ni/NZ catalysts were determined by XRD analysis. The XRD patterns of the parent NZ and that after immobilization of Ni are shown in Fig. 1. According to the results, clinoptilolite ($2\theta = 13.68^\circ, 26.78^\circ, 30.12^\circ$) and mordenite ($2\theta = 19.74^\circ, 22.42^\circ, 25.82^\circ, 27.92^\circ$) phases were dominant in the NZ structure and no peaks indicating phases of SiO₂ and Al₂O₃ were detected. The structure of zeolites consists of silicon, aluminum and oxygen that form a framework with cavities and channels inside where cations, water or small molecules may reside. A high peak intensity at $2\theta=26.78^\circ$ indicated that the parent NZ compose of moderite as its main constituent mineral with some existence of clinoptilolite.

When compared with the pattern of Ni/NZ and Ni/NZ-HT catalysts, no change in the value of 2θ were observed for the modified NZ, however, the peak intensity increased after the immobilization of Ni. This is suggested due to the calcination and hydrogen treatment processes which may remove impurities in the NZ framework. These results show that the

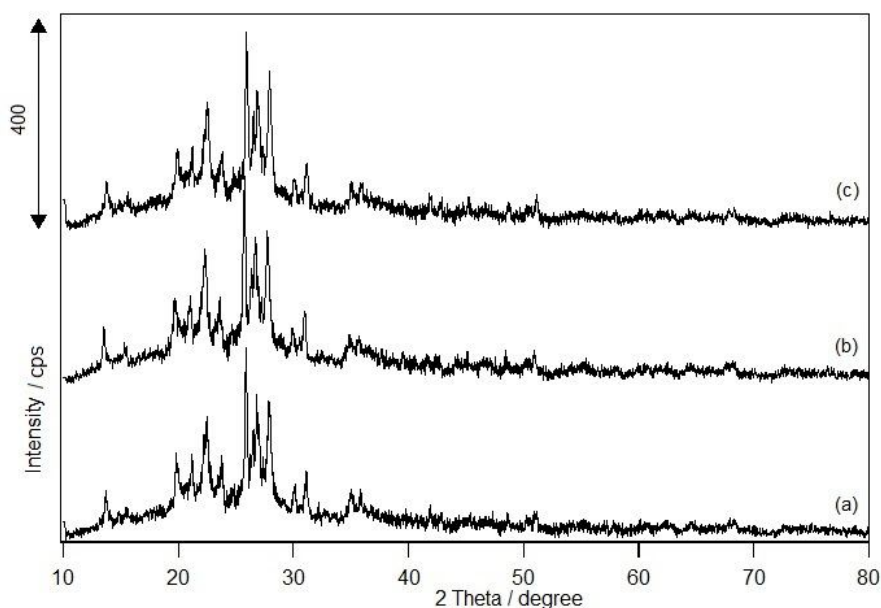


Fig 1. XRD patterns of Ni/NZ catalysts. (a) NZ, (b) Ni/NZ, (c) Ni/NZ-HT

Table 3. Conversion of citronellal and its derivatives to menthol using various catalysts

Entry	Catalyst	Conversion (%)	Yield (\pm)-isopulegol (%)	Yield (-)-menthol (%)	Yield others(%)	Selectivity (-)-menthol (%)
1 ^a	Ni/NZ	100	7	0	93	0
2 ^b	Ni/NZ	90	4	0	86	0
3	Ni/NZ-HT	97	12	0	85	0
4 ^c	Ni/NZ-HT	24	-	9	16	36
5 ^a	Ni/ZSM5	65	22	4	39	6
6	Ni/ZSM5-HT	48	8	0	40	0
7 ^d	Ni/ZSM5-HT	77	14	2	61	3
8	Blank	0	0	0	0	0

Reaction conditions: (\pm)-citronellal (5 mmol), catalyst (0.1 g), cyclohexane (5 mL), 70°C, 6h, 2 MPa H₂.
^areaction time: 24 h, ^btoluene as solvent, ^cisopulegol as reactant, ^dcatalyst: 0.2 g.

structure of the modified zeolites remains intact even after the loading of Ni metals. Meanwhile no peaks related to the Ni and NiO phase were found in the diffractograms, indicating that the Ni metals were highly dispersed on the Ni/NZ and Ni/NZ-HT catalysts.

Conversion of (\pm)-Citronellal and Its Derivatives to (-)-Menthol

Conversion of (\pm)-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 3. 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 by products are predicted to be mainly citronellol and 3,7-dimethyl octanol (Fig 2). 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 Bronsted acid and high Lewis acid sites will give a high selectivity in the cyclization reaction of citronellal to isopulegol (Chuah, *et.al.*, 2008).

To determine whether the Ni metal active site in the catalyst was effective for the hydrogenation reaction, catalytic

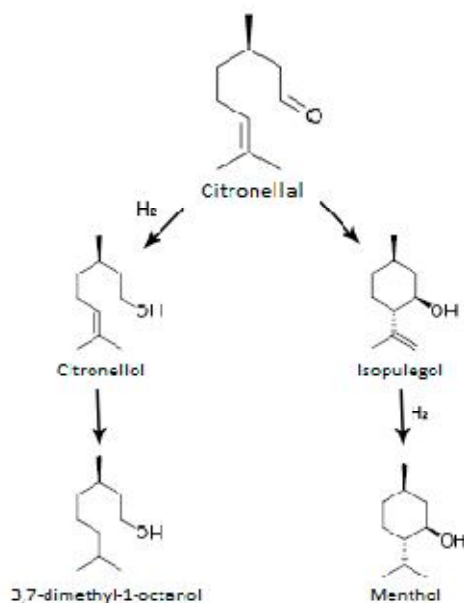


Fig 2. Products derived from citronellal

reactions using (\pm)-citronellal and its derivative (\pm)-isopulegol as the starting material were conducted using Ni/NZ-HT catalyst.

The amount of (-)-menthol obtained as a reaction product were analyzed using a gas chromatography equipped with a DB-5MS column by which the detection method gave an adequate difference of peak retention time between (+)-menthol and (-)-menthol. Results reveal that no yield of (-)-menthol was obtained when citronellal was used as the reactant (entry 3). On the other hand, 9% yield of (-)-menthol could be obtained from isopulegol with 24% conversion giving 36% 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 was still low. In the cases of Ni/ZSM5 and Ni/ZSM5-HT catalysts, lower conversions of 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 revealed no 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.

The plausible mechanism for the conversion of (\pm)-citronellal to (-)-menthol using zeolite catalyst is assumed to occur through several steps. At first is the protonation of the carbonyl group of citronellal on the catalytic zeolite acid site, followed by intramolecular rearrangement of citronellal to form a more stable carbocation, which there by generates isopulegol. Secondly, adsorption of hydrogen molecules and subsequent hydrogenation of the alkene group of isopulegol on the catalytic Ni metal site. And finally desorption of the desired menthol product from the bifunctional Ni zeolite catalyst.

4. CONCLUSIONS

Conversion of (\pm)-citronellal and its derivatives to (-)-menthol proceeded using bifunctional Ni zeolite catalysts. These catalysts were prepared from natural zeolite (NZ) and synthetic zeolite ZSM-5 (ZSM-5) by immobilization of Ni using a simple cation-exchange procedure. Calcination and hydrogen treatment procedures were able to significantly increase the surface area and pore volume of NZ based catalysts whereas negligible changes in the properties were observed for that of ZSM-5. Ni/NZ-HT catalyst showed good activity of 24% conversion of a (\pm)-citronellal derivative yielding 9% of (-)-menthol and 36% selectivity whereas a 4% yield of (-)-menthol and 6% selectivity was seen in the direct conversion of 65% (\pm)-citronellal using the Ni/ZSM5 catalyst. Optimization of the reaction parameters are essential to enhance the yield of (-)-menthol is under further investigation. Therefore, low cost Ni zeolite catalysts were able to demonstrate promising competitive catalytic activity with other supported metal catalysts which generally yields the racemic (\pm)-menthol from (\pm)-citronellal and are potential materials for the synthesis of flavor chemicals from citronella oil.

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