ORIGINAL ARTICLES

One Pot Transformation of Citronellal to Menthol over Ni/γ-al$_2$o$_3$

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ABSTRACT

Citronella oil from *Cymbopogon winterianus* is widely produced in Indonesia (Java type). A way to increase the value of this product is to transform citronellal contained in the oil into menthol, one of the most sought after fragrance products. The one pot citronellal to menthol transformation is also a war horse of tandem reactions over heterogeneous catalysts. Here we wish to report our results in the one pot transformation of citronellal into menthol over a Ni/Al$_2$O$_3$ catalyst. While alumina showed to be a poor catalyst for the transformation of citronellal into isopulegol, ZnBr$_2$ modified alumina allowed to obtain very fast formation of isopulegol. However, when Ni was supported on the modified alumina and used under hydrogenation conditions only isopulegol was obtained even after long reaction times. On the contrary a 10% Ni/ Al$_2$O$_3$ catalyst showed fairly good activity. These results can be ascribed to very big differences in Ni particle size and to reduced surface area of the Zn containing catalyst.

*Key words:* citronellal, isopulegol, menthol

Introduction

Citronella (*Cymbopogon winterianus* Jowitt, family: Poaceae) is a multi-harvested, high-demand, aromatic crop cultivated in a number of countries. The essential oil isolated from freshly harvested or partially dried shoot biomass is extensively used in the fragrance industry and for extraction of the aroma chemicals citronellal, citronellol and geraniol.

Citronellal (3,7-dimethyl-6-octen-1-al) 1, represents a raw material of great interest for the preparation of several fine chemicals. The chemoselective hydrogenation of the carbonyl group of citronellal leads to the unsaturated alcohol, citronellol, 5 which is widely employed in perfumery (Milone *et al.,* 1999). Moreover, from the isomerisation of citronellal on acid catalysts, the unsaturated cyclic alcohols (isopulegols) 2, can be obtained (Yongzhong *et al.,* 2005; Arvela *et al.,* 2004; Milone *et al.,* 2002; Chuah *et al.,*2001; Nie *et al.,* 2006; Yadav and Nair, 2000; Iosif *et al.,* 2004; Milone *et al.,* 2000; Neatu *et al.,* 2009). The isopulegol are useful intermediates for the synthesis of the corresponding saturated alcohols (menthols), 3.

Menthols 3, are generally obtained in two step through the isomerisation of citronellal to isopulegols on acid catalysts (Yongzhong *et al.,* 2005; Arvela *et al.,* 2004; Milone *et al.,* 2002; Chuah *et al.,*2001; Nie *et al.,* 2006; Yadav and Nair, 2000; Iosif *et al.,* 2004; Milone *et al.,* 2000; Neatu *et al.,* 2009) followed by their hydrogenation (Scheme 1). In the industrial process for (-)-menthol, 3a, production (Tagasako process), the isomerisation of (+)-citronellal is carried out in the presence of ZnBr$_2$. Under these conditions, (-)-isopulegol, 2a, yields up to 92% have been reported (Misono and Noijri, 1990). The cyclic alcohol is then separated from the reaction mixture and hydrogenated to the corresponding saturated alcohol (-)-menthol, 3a. It is reported that the acid catalyst ZnBr$_2$ is employed as aqueous solution (Misono and Noijri, 1990), however, powdered anhydrous ZnBr$_2$ has been found to be very selective towards the formation of (-)-isopulegol (Nakatani and Kawashima, 1978). One of the main drawbacks in the use of solid ZnBr$_2$ is the difficulty to maintain the salt under anhydrous conditions being highly hygroscopic, hence, precautions are required in the storage and handling ZnBr$_2$ if it is used in the solid state.

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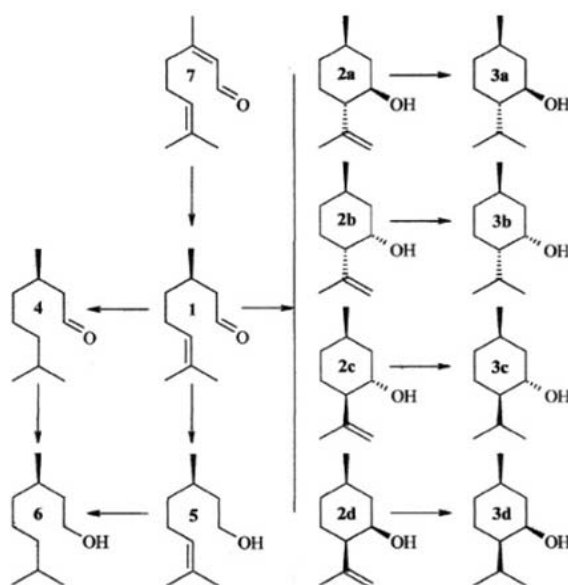
Scheme 1.

Therefore, the synthesis of heterogeneous catalysts that combine high stereoselectivity to (-)-isopulegol and easy of handling can be a strategic tool for the optimization of the (-)-menthol synthetic process.

Cyclisation of citronellal on several solid acid catalysts has been investigated (Yongzhong *et al.,* 2005; Arvela *et al.,* 2004; Milone *et al.,* 2002; Chuah *et al.,*2001; Nie *et al.,* 2006; Yadav and Nair, 2000; Iosif *et al.,* 2004; Milone *et al.,* 2000; Neatu *et al.,* 2009), but few studies deal with the distribution of the stereoisomers formed during the reaction on γ-Al_2O_3 and γ-Al_2O_3 supported catalysts. A main goal of this research is to develop a catalytic system which is able to synthesize menthols from citronellal in one single step by carrying out the reaction in the presence of isomerisation and hydrogenation sites on γ-Al_2O_3 as a supported catalyst.

Study that concern on γ-Al_2O_3 as a supported catalysts have investigated (Ravasio *et al.,* 2006), during the hydrogenation of very low value mints oils, namely, dementholized oil. Among the different Cu catalysts, they reported that Cu/γ-Al_2O_3 showed the best activity and selectivity towards a mixture of menthols, 3, while stereoselectivity towards the valuable isomer (-)-menthol, 3a can be improved by selectively dehydrogenating the products mixture. In the hydrogenation of pulegone and *pennyroyal oil*, Cu/γ-Al_2O_3 catalyst also showed an unprecedented activity allowing complete transformation of the substrate into menthols under very mild experimental conditions (1 atm H_2, 90°C).

Study the isomerisation of (+)-citronellal with very high stereoselectivity value to (-)-isopulegol also investigated with Lewis acid such as $ZnBr_2$, $ZnCl_2$, $Zn(NO_3)_2$, $FeCl_3$ and $SnCl_2$ supported on SiO_2 (Milone *et al.,* 2000) Among the salts investigated, $ZnBr_2$ was the most effective in terms of catalytic activity and selectivity to (-)-isopulegol, 2a. The catalytic activity and the selectivity to (-)-isopulegol, 2a was found to increase with the Zn loading and the temperature of calcinations. The maximum selectivity of (-)-isopulegol, 2a obtained on $ZnBr_2$ supported catalysts was 86% (Milone *et al.,* 2000).

Here we wish to report our investigation on the catalytic activity of $ZnBr_2$/γ-Al_2O_3, Ni/γ-Al_2O_3 and Ni/$ZnBr_2$/γ-Al_2O_3 catalysts in the isomerisation, hydrogenation and one pot transformation of (+)-citronellal to menthol. We have also decided to elucidate the influence of the morphology of the catalysts in order to get information on the nature of the catalytic active sites.

Experimental section:

Materials:

General remarks: γ-Al_2O_3 (BET=190 m^2/g, PV=1.214 cm^3/g), $ZnBr_2$, Ni ($NO_3)_2$.$6H_2O$, and methanol, was purchased from MERCK, (*R*)-(+)-Citronellal (>90%) was obtained from fractional distilation under reduced pressure towards Citronella Oil that purchased from Cilacap, Central of Java.

Instrumentation:

X-Ray Diffractometer (Philips X'Pert), BET Surface Area Analyzer (Quantachrome NovaWin2), Transmission Electron Microscope (EF-TEM Leo912AB), FTIR Spectrometer (Shimadzu, FTIR-8201 PC), Gas Chromatography (GC-Agilent 7890)

Procedure:

Catalyst preparation:

The $ZnBr_2/\gamma\text{-}Al_2O_3$ catalyst was prepared by adding the support γ-alumina to a methanol solution containing the proper amount of the Zn salt. The solvent was slowly removed by rotary evaporation at 35 °C for 1 h. Catalyst was dried at 120 °C for 2 h, then calcined at 400 °C for 3 h, unless otherwise specified (Milone *et al.,* 1999; 2002).
The Ni/γ-alumina catalyst was prepared by adding the support γ-Al_2O_3 to a methanol solution containing the proper amount of the $Ni(NO_3)_2.6H_2O$ salt. The solvent was slowly removed by rotary evaporation at 35 °C for 1 h. Catalyst was dried at 120 °C for 2 h, then calcined at 500 °C for 3 h. Before hydrogenation activity measurements the Ni/ γ-alumina catalyst were reduced for 3 h at 500 °C.
The $Ni/ZnBr_2/\gamma\text{-}Al_2O_3$ catalyst was prepared by adding the $ZnBr_2/\gamma\text{-}Al_2O_3$ catalyst to a methanol solution containing the proper amount of the $Ni(NO_3)_2.6H_2O$ salt. The solvent was slowly removed by rotary evaporation at 35 °C for 1 h. Catalyst was dried at 120 °C for 2 h, then calcined at 500 °C for 3 h. Before hydrogenation activity measurements the Ni/ γ-alumina catalyst was reduced for 3 h at 500 °C.

Catalyst characterization:

X-ray diffraction patterns were recorded by using a Philips X'Pert, operated at 40 kV and 30 mA using Ni-filtered Cu Kα radiation at a step scan mode (2 step, 0.02°; acquisition time, 1 sec. per step) with a 1° divergence and scatter slit and a 0.1 mm receiving slit. Powder sampling were mounted on Plexiglas holders. Specific surface area and porosity data were determined by adsorption-desorption of di-nitrogen at 77 K using Quantachrome NovaWin2. Pore size distribution and pore volume were derived from the desorption isotherm at $P/Po \geq 0.3$
Transmission Electron Microscope (TEM) images of samples were obtained on a EF-TEM Leo912AB 120 KV microscope equipped with Energy Filter and EELS spectrometer. The powder samples have been grinded and ultrasound dispersed in isopropanol. A drop of the suspension has been deposited on the carbon grid which, after solvent evaporation under vacuum, has been inserted in the column of the Transmission Electron Microscope. Pictures have been taken at 14.000-50.000x magnifications, spanning wide regions of several support grains in order to provide a well representative map of the catalyst system.
The quantitative determination of Bronsted and Lewis acid sites in catalysts was performed using infrared spectroscopy with pyridine as a probe molecule.

Experimental setup:

The bare supports were treated at 270 °C for 20 min in air and for 20 min under reduced pressure at the same temperature; the catalysts underwent a further treatment of reduction at 270 °C with H_2. The substrate (0.1 g) were dissolved in toluene dehydrated (8 mL) and the solution transferred under N_2 into glass reaction vessel where the catalyst (0.1 g) had been previously treated. Reactions were carried out at 90 °C with magnetic stirring under N_2 or H_2. Product distribution and yields were determined by GC and by H^{1}NMR of the raw reaction mixture.

Product characterization:

Reaction mixture was analyzed by GC using a crosslinked 5% phenyl methyl silicone (HP 5 M.S., 30 m) or a nonbonded, poly (80% biscyanopropyl/20% cyanopropylphenyl siloxane; SP2330, 60 m) capillary column. Reaction products were identified through their MS (HP 5971 series) and 1H NMR spectra (Bruker 300 MHz); stereoselectivities were evaluated by GC and ^{1}H NMR.

Results and discussion

Characterization of the Catalysts:

The X-ray powder diffraction patterns of catalysts were similar to those reported in the literature and have shown the absence of resolved reflections. It was inferred from the XRD data that the all catalysts were highly phase pure having structures of γ-Al_2O_3 with the precursor is present in a high amount. It must be assumed that amorphous $ZnBr_2$ and Ni noble metal is present on the surface of the support in the form of mono or multilayers (Ravasio *et al.*, 2006). The XRD pattern of all catalysts are given in Fig.1
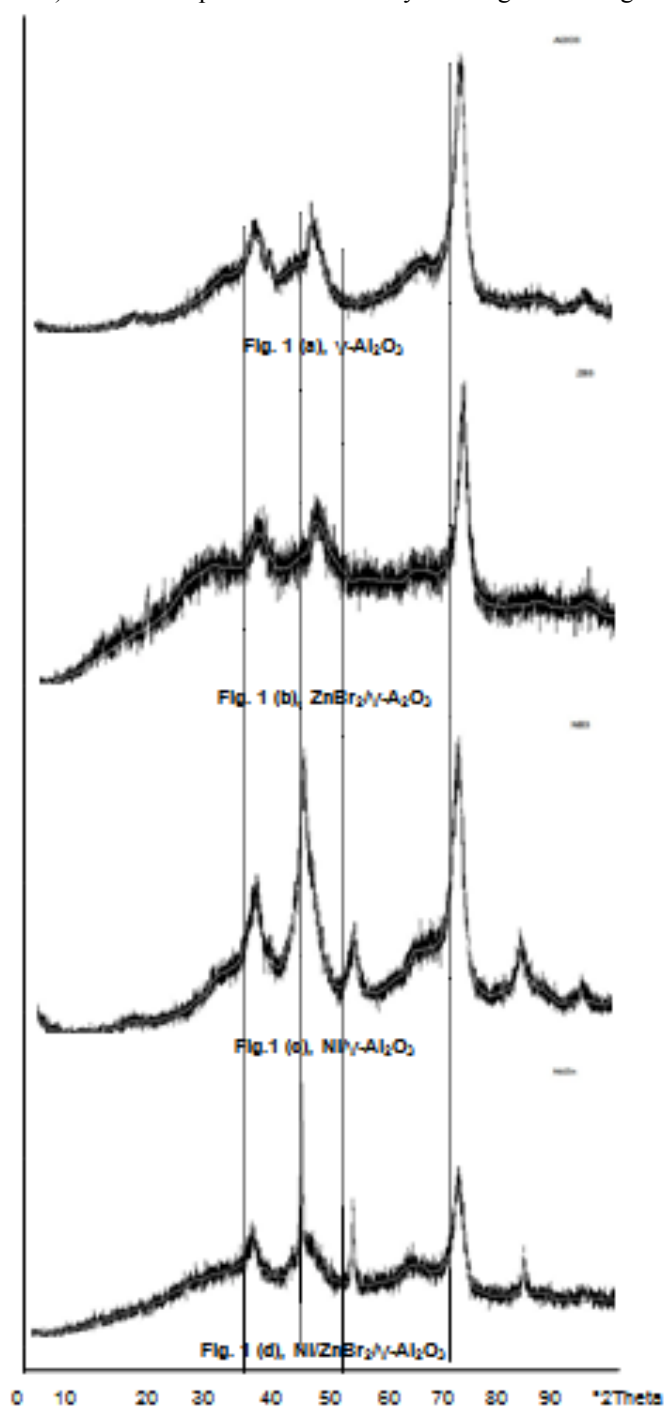
**Fig. 1:** X-Ray powder diffraction pattern of catalysts

The specific surface areas of the catalysts measured by nitrogen adsorption are shown in Table 1. The catalysts used show a S_{BET} ranging between 60.25 and 120.50 m^2/g and a pore-size distribution varying between 22.45 and 29.30 nm. The highest specific surface area was observed for γ-Al$_2$O$_3$ support and after which the specific surface areas decreased in the following order : Ni/γ-Al$_2$O$_3$ > ZnBr$_2$/γ-Al$_2$O$_3$ > Ni/ZnBr$_2$/γ-Al$_2$O$_3$. The addition of ZnBr$_2$ and/or Ni leads to a slight decrease of the surface area and pore volume. The Zn and Ni loading determined by X-Ray Fluoresency, ranges between 7.4 and 10.7 wt.%. The decrease of the surface area and pore volume of the ZnBr$_2$ and Ni supported γ-Al$_2$O$_3$ can be attributed to ZnBr$_2$ and Ni filling up the pores of the support (Misono and Noijri, 1990)

Table 1: Morphological properties of γ-Al$_2$O$_3$ support and catalysts

| Catalysts	S.A (m2/g)	Mean pore diameter (nm)	Pore volume (cm3/g)	Zn[a] (wt%)	Ni[a] (wt%)
γ-Al$_2$O$_3$	120.50	29.30	0.25	-	-
ZnBr$_2$/γ-Al$_2$O$_3$	66.74	24.33	0.14	9.7	-
Ni/γ-Al$_2$O$_3$	115.85	27.95	0.22	-	8.6
Ni/ZnBr$_2$/γ-Al$_2$O$_3$	60.25	22.45	0.13	10.7	7.4

[a] Determined by X-Ray Fluoresency

TEM coupled with the elemental analysis (EELS) of the catalysts have been also performed. TEM micrograph pictures of ZnBr$_2$/γ-Al$_2$O$_3$ have shown that the morphological structure of the catalyst support is differentially oriented (Fig.2a), thus indicating that the ZnBr$_2$ is widespread onto the surface. TEM micrograph pictures of Ni/γ-Al$_2$O$_3$ have been performed by single thin of γ-Al$_2$O$_3$ crystal with oriented mesopores (pore size : 16 nm) which occupied with Ni metal particles (size : 7 nm) inside the pores (Fig. 2b). Then, thin section of Ni/ZnBr$_2$/γ-Al$_2$O$_3$ catalyst have shown that almost all of pores on the surface of γ-Al$_2$O$_3$ crystal covered by small Zn particles and occurred the enlargement (agglomeration) of Ni metal particles (size : 59 nm) (Fig.2c)

(a)   (b)   (c)
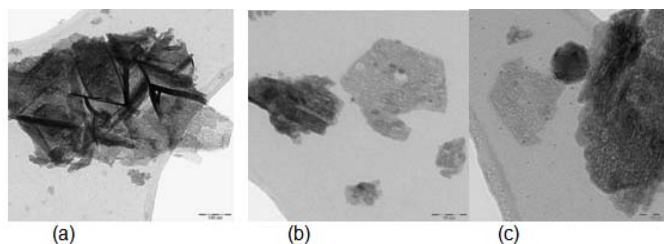
Fig. 2: (a). Micrograph picture of ZnBr$_2$/γ-Al$_2$O$_3$, (b). Micrograph picture of Ni/γ-Al$_2$O$_3$, (c). Micrograph picture of Ni/ZnBr$_2$/γ-Al$_2$O$_3$

The amount of Bronsted and Lewis acid sites was measured by FTIR with pyridine as a probe molecule. The adsorption bands of pyridinium ion of adsorbed pyridine corresponding Bronsted acidity is at 1543-1545 cm^{-1}, whereas the adsorbed pyridine is on Lewis acid sites at 1452-1458 cm^{-1} (May *et al.*, 2007). It should be pointed out that in case of Ni/ZnBr$_2$/γ-Al$_2$O$_3$ catalysts, two peaks appeared corresponding to lewis acidity, i.e., the peaks at 1452 and 1458 cm^{-1} (Fig.3)
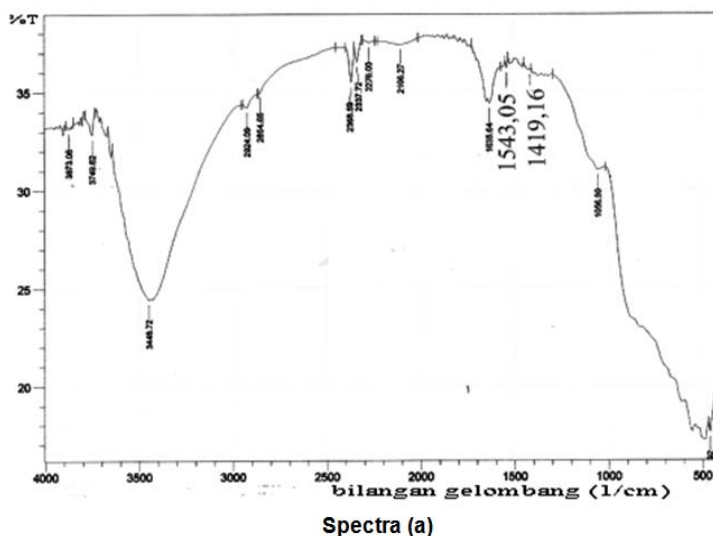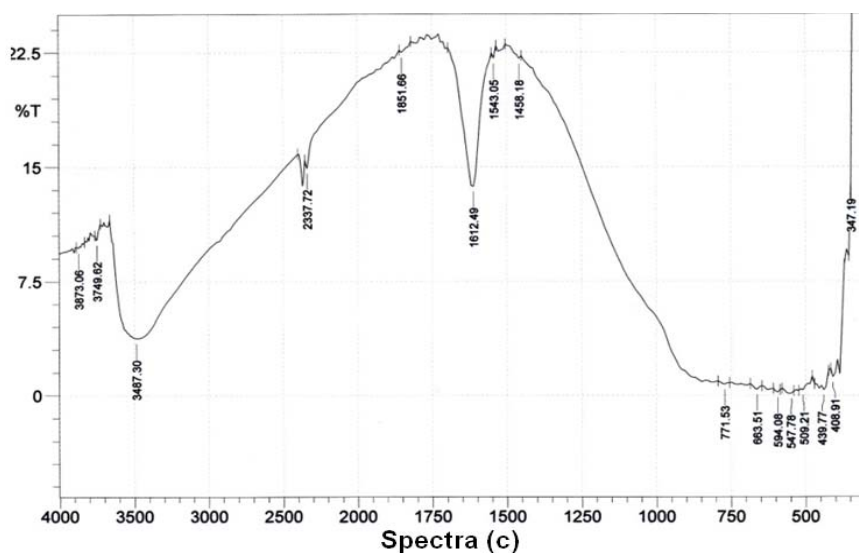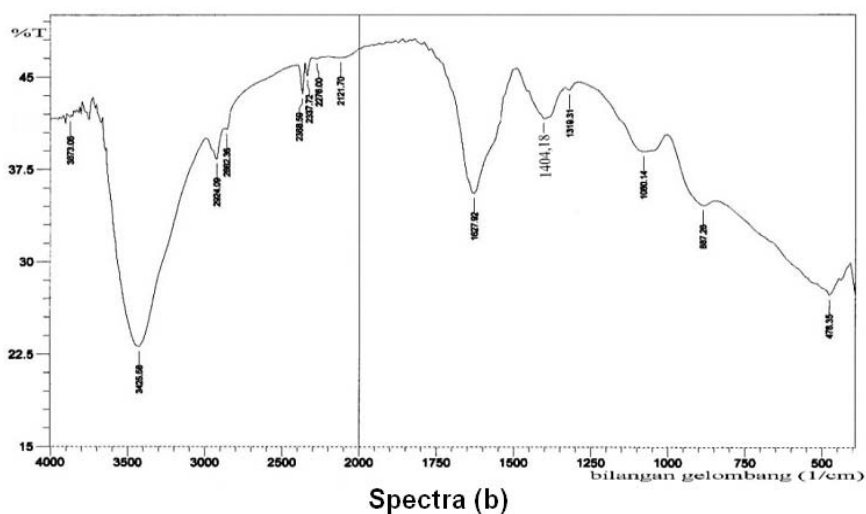

Spectra (a)

Fig. 3: FTIR spectra with pyridine adsorbed for (a). ZnBr₂/γ-Al₂O₃, (b). Ni/γ-Al₂O₃, (c). Ni/ZnBr₂/γ-Al₂O₃

Catalytic activity:

Results obtained with different catalysts are listed in Table 2. Under the experimental condition used (1 atm, 90 °C), ZnBr₂/γ-Al₂O₃, which carried out under N₂, (+)-citronellal is converted only to the isopulegol stereoisomer in all range of conversion investigated (entry 1-2). No other reaction products were detected. On the acidified supports, the only reaction products were isopulegols due the lack of hydrogenation sites.

Table 2: Cyclization and Hydrogenation of (+)-citronellal in the presence of different catalysts

Entry	Catalyst	t (h)	Gas	1	2	3
Initial composition				83.12	15.17	-
1	ZnBr₂/γ-Al₂O₃	1.5	N₂	-	91.48	-
2	ZnBr₂/γ-Al₂O₃	2.5	N₂	-	92.58	-
3	Ni/γ-Al₂O₃	1.5	H₂	-	92.82	0.63
4	Ni/γ-Al₂O₃	19	H₂	-	48.93	40.32
5	Ni/γ-Al₂O₃	40	H₂	-	3.73	86.77
6	Ni/γ-Al₂O₃	1.5	N₂	66.53	28.24	-
7	Ni/γ-Al₂O₃	1.5 + 1.5	N₂ + H₂	58.92	29.91	-
8	Ni/γ-Al₂O₃	1.5	H₂	58.16	32.88	-
9	Ni/γ-Al₂O₃	25.5	H₂	-	3.81	84.03
10	Ni/ZnBr₂/γ-Al₂O₂	1.5	H₂	-	97.65	-
11	Ni/ZnBr₂/γ-Al₂O₂	3.5	H₂	-	97.00	-
12	Ni/ZnBr₂/γ-Al₂O₂	25	H₂	-	91.58	-

A further step of reaction was continued by using the Ni/γ-Al$_2$O$_3$ catalysts to hydrogenation of the C=C bonds. (entry 3-5). Reaction mixture product of isopulegol isomers firstly separated from residu of ZnBr$_2$/γ-Al$_2$O$_3$ catalyst and changed by Ni/γ-Al$_2$O$_3$ catalysts. Next reaction carried out under H$_2$. The best product as function of hydrogenation C=C bonds on isopulegol obtained in very mild condition (1 atm, 90 ºC) with the menthol toward 86.77 %.

In contrast, when Ni/γ-Al$_2$O$_3$ catalysts used are only slightly active for the isomerisation of (+)-citronellal when reaction carried out under N$_2$, (yield only 28.24%) (entry 6). The presence of H$_2$ leads only slighty enhancement of the catalytic activity, towards isopulegol isomers (entry 7). To clarify this point, the next investigated catalysts (entry 8-9), have been used in reaction carried out directly under H$_2$. Reaction carried out under H$_2$ can be isomerised to the unsaturated cyclic products, isopulegols. These results indicate that the morphological parameters of the solids do not influence the activity and selectivity of the reaction. Mechanism of the reaction is unclear and probably both Lewis and Bronsted acidic sites play a role in the catalytic pathway. Isopulegol exists as four different stereoisomers. In this work, we have not been separated and therefore we are indicated as "isopulegols". As further reduction step, the isopulegols are quite difficult to convert into the corresponding saturated cyclic alcohols, menthols (entry 8). These results are a confirmation that the contribution of the strongly adsorbed H$_2$ to the catalytic activity is very important.

The reaction has to show an isomerisation rate higher than hydrogenation rate in order to carry out first quantitative isomerisation of citronellal to isopulegol (entry 8), then the hydrogenation of the latter to the corresponding menthols up to 84.03 % (entry 9). Formation of open chain hydrogenation of the C=C and C=O bonds of (+)-citronellal to produce citronellol, **5** and 3,7-dimethyl octanal, **6** was avoided. The reduction of the carbon-carbon double bond is quite unusual; thus, it is well known that nickel catalysts exhibit very high chemoselectivity towards reduction of carbonyl groups in the presence of olefinic bonds and that only carbon-carbon double bonds conjugated with a carbonyl group are easily hydrogenated even in the presence of isolated double bonds. Best activity were obtained with the menthols up to 84.03 % (entry 9).

On the basis of these previous results, the next step was develop a catalytic system that able to synthesis menthols from (+)-citronellal in one single step, by carrying out the reaction in the presence of stereoselctive isomerisation and hydrogenation sites (entry 10-12). The results obtained have shown that bifunctional catalyst Ni/ZnBr$_2$/γ-Al$_2$O$_3$ just only effective with higher rate on isomerisation of citronellal to isopulegol than the hydrogenation of the latter to corresponding menthols. The yield to isopulegols was about 97.65 % (entry 10). At present the mechanism through which the Lewis acid sites favour the selective synthesis of isopulegol is not understood and further work is necessary to clarify this point.

Conclusion:

The results reported in this study have pointed out that it is possible to modify the course of the cyclization and hydrogenation of (+)-citronellal over ZnBr$_2$ and Ni supported catalysts. On more acid catalysts, ZnBr$_2$/γ-Al$_2$O$_3$ and Ni/ZnBr$_2$/γ-Al$_2$O$_3$, isopulegols are preferentially formed as primary products.

A Ni/γ-Al$_2$O$_3$ has shown to be an excellent catalyst for the one step hydrogenation of (+)-citronellal under extremely mild condition. Its use allows to produce menthols with fairly good stereoselectivity.

Acknowledgements

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687

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