

CYCLIZATION AND HYDROGENATION OF (+)-CITRONELLAL TO MENTHOLS OVER $ZnBr_2$ AND Ni CATALYSTS SUPPORTED ON $\gamma-Al_2O_3$

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Received March 10, 2010; Accepted June 4, 2010

ABSTRACT

Two steps transformation of (+)-citronellal, cyclization and hydrogenation, on $ZnBr_2/\gamma-Al_2O_3$ and $Ni/\gamma-Al_2O_3$ catalyst have been realized with the selectivity to cyclization products (isopulegols) was very high (yield up to ~92.58%) over $ZnBr_2/\gamma-Al_2O_3$ under mild condition (90 °C and 1 atm nitrogen atmosphere) with high Brønsted acid concentration, while at the same time very low cyclization rates were achieved over $Ni/\gamma-Al_2O_3$ with low or no Brønsted acidity, respectively. The highest cyclization rates were observed over $Ni/ZnBr_2/\gamma-Al_2O_3$ under mild condition (90 °C and 1 atm hydrogen atmosphere). The second step transformation towards cyclization products, hydrogenation to menthols, was performed with $Ni/\gamma-Al_2O_3$ under hydrogen atmosphere. Surprisingly the one-step transformation of (+)-citronellal into menthols was investigated over $Ni/\gamma-Al_2O_3$ with yield ~84% under hydrogen atmosphere (90 °C, 1 atm) by exploiting the presence of acidic and hydrogenation sites on the catalyst surface. On the $Ni/\gamma-Al_2O_3$ catalyst it was found that the cyclization of (+)-citronellal to isopulegols occurs on the surface of the support. In the presence of the noble metal, the isopulegols are further hydrogenated to the menthols.

Keywords: cyclization, hydrogenation, citronellal, isopulegol, menthol

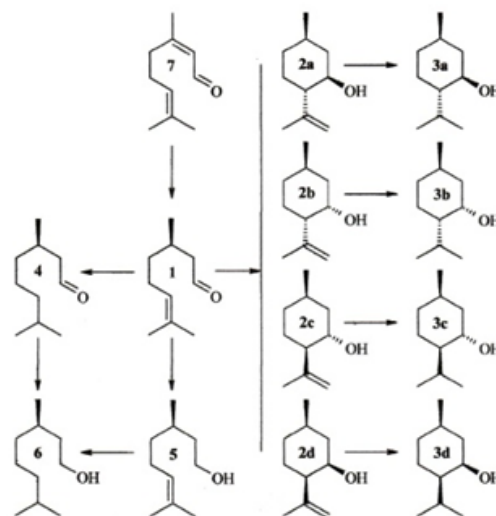
INTRODUCTION

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 [1]. Moreover, from the isomerisation of citronellal on acid catalysts, the unsaturated cyclic alcohols (isopulegols) **2**, can be obtained [2-10]. The isopulegols 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 [2-10] 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 [11]. 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 [11], however, powdered anhydrous $ZnBr_2$ has been found to be very selective towards the formation of (-)-isopulegol [12]. 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.



Scheme 1. Cyclization and hydrogenation of (+)-citronellal

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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 [2-10], but few studies deal with the distribution of the stereoisomers formed during the reaction on γ -Al₂O₃ and γ -Al₂O₃ 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 -Al₂O₃ as a supported catalyst.

Study that concern on γ -Al₂O₃ as a supported catalysts have investigated [13], during the hydrogenation of very low value mints oils, namely, dementholized oil. Among the different Cu catalysts, they reported that Cu/ γ -Al₂O₃ 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 -Al₂O₃ catalyst also showed an unprecedented activity allowing complete transformation of the substrate into menthols under very mild experimental conditions (1 atm H₂, 90 °C).

Study the isomerisation of (+)-citronellal with very high stereoselectivity value to (-)-isopulegol also investigated with Lewis acid such as ZnBr₂, ZnCl₂, Zn(NO₃)₂, FeCl₃ and SnCl₂ supported on SiO₂ [9]. Among the salts investigated, ZnBr₂ 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 ZnBr₂ supported catalysts was 86% [9].

Here we wish to report our investigation on the catalytic activity of ZnBr₂/ γ -Al₂O₃, Ni/ γ -Al₂O₃ and Ni/ZnBr₂/ γ -Al₂O₃ catalysts in the isomerisation and hydrogenation of (+)-citronellal. 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 -Al₂O₃ (BET=190 m²/g, PV=1.214 cm³/g), ZnBr₂, Ni (NO₃)₂.6H₂O, and methanol, was purchased from MERCK, (*R*)-(+)-Citronellal (>90%) was obtained from fractional distillation 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 ZnBr₂/ γ -Al₂O₃ 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 [1,4].

The Ni/ γ -alumina catalyst was prepared by adding the support γ -Al₂O₃ to a methanol solution containing the proper amount of the Ni(NO₃)₂.6H₂O 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/ZnBr₂/ γ -Al₂O₃ catalyst was prepared by adding the ZnBr₂/ γ -Al₂O₃ catalyst to a methanol solution containing the proper amount of the Ni(NO₃)₂.6H₂O 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 K α radiation at a step scan mode (2 θ 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 $P/P_0 \geq 0.3$

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

Table 1. Morphological properties of γ -Al₂O₃ support and catalysts

Catalysts	S.A (m ² /g)	Mean pore diameter (nm)	Pore volume (cm ³ /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

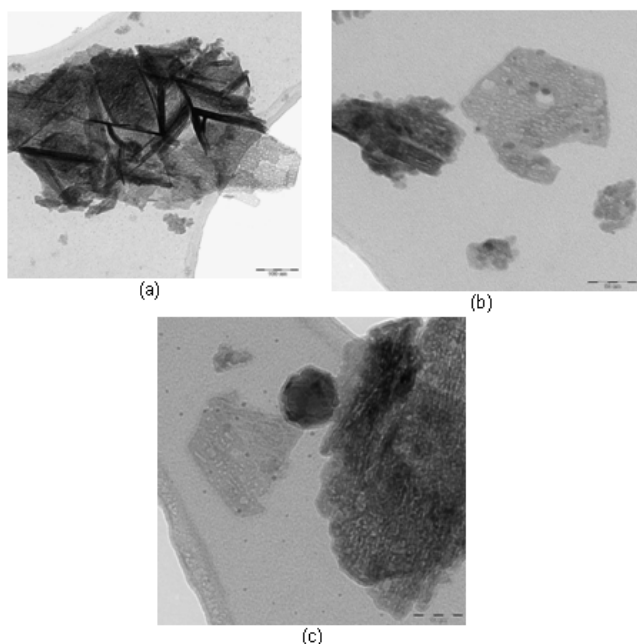


Fig 1. (a). Micrograph picture of ZnBr₂/ γ -Al₂O₃, (b). Micrograph picture of Ni/ γ -Al₂O₃, (c). Micrograph picture of Ni/ZnBr₂/ γ -Al₂O₃

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 Brønsted 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 H₂. The substrate (0.1 g) were dissolved in toluene dehydrated (8 mL) and the solution transferred under N₂ 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 N₂ or H₂. Product distribution and

yields were determined by GC and by H¹NMR 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 ¹H NMR.

RESULT 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 -Al₂O₃ with the precursor is present in a high amount. It must be assumed that amorphous ZnBr₂ and Ni noble metal is present on the surface of the support in the form of mono or multilayer [13]. The XRD patterns of all catalysts are given in Fig. 1.

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 m²/g and a pore-size distribution varying between 22.45 and 29.30 nm. The highest specific surface area was observed for γ -Al₂O₃ support and after which the specific surface areas decreased in the following order: Ni/ γ -Al₂O₃ > ZnBr₂/ γ -Al₂O₃ > Ni/ZnBr₂/ γ -Al₂O₃. The addition of ZnBr₂ 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 ZnBr₂ and Ni supported γ -Al₂O₃ can be attributed to ZnBr₂ and Ni filling up the pores of the support [11]

TEM coupled with the elemental analysis (EELS) of the catalysts have been also performed. TEM micrograph pictures of ZnBr₂/ γ -Al₂O₃ have shown that the morphological structure of the catalyst support is differentially oriented (Fig. 2a), thus indicating that the

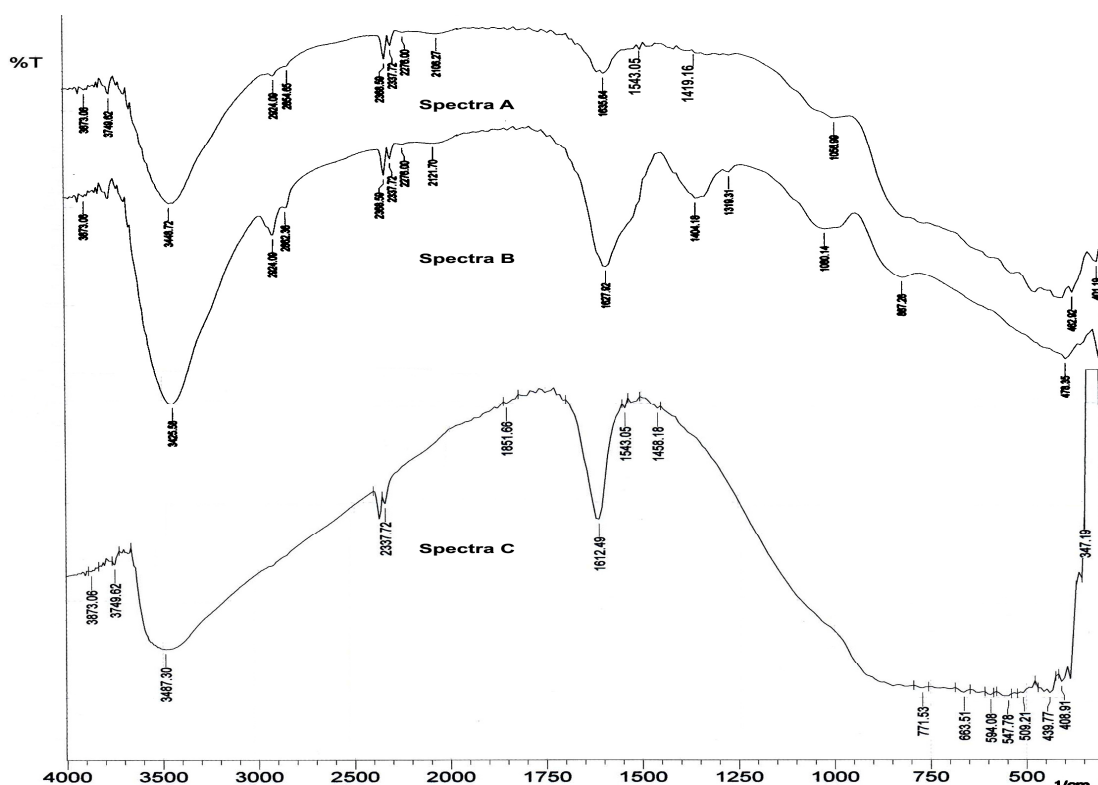


Fig 3. FTIR spectra with pyridine adsorbed for (a). $\text{ZnBr}_2/\gamma\text{-Al}_2\text{O}_3$, (b). $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$, (c). $\text{Ni}/\text{ZnBr}_2/\gamma\text{-Al}_2\text{O}_3$

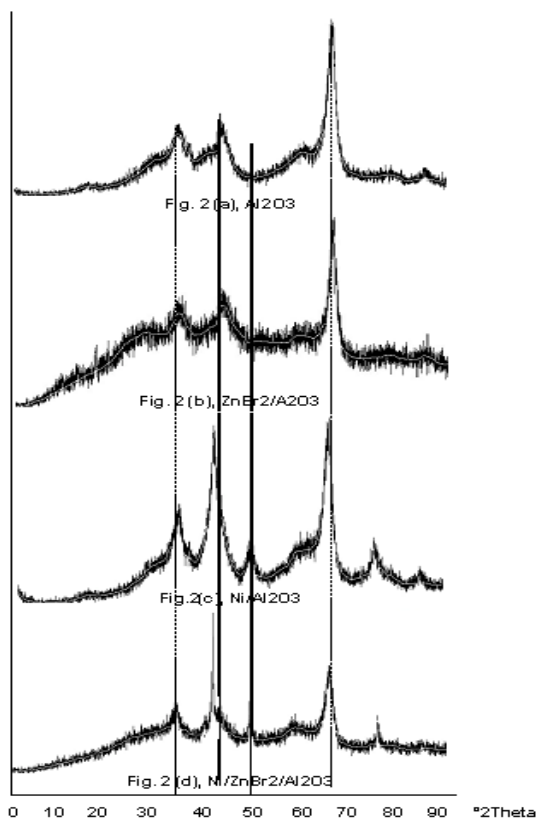


Fig 2. X-Ray powder diffraction pattern of catalysts

ZnBr_2 is widespread onto the surface. TEM micrograph pictures of $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ have been performed by single thin of $\gamma\text{-Al}_2\text{O}_3$ 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 $\text{Ni}/\text{ZnBr}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst have shown that almost all of pores on the surface of $\gamma\text{-Al}_2\text{O}_3$ crystal covered by small Zn particles and occurred the enlargement (agglomeration) of Ni metal particles (size: 59 nm) (Fig. 2c)

The amount of Brønsted and Lewis acid sites was measured by FTIR with pyridine as a probe molecule. The adsorption bands of pyridinium ion of adsorbed pyridine corresponding Brønsted acidity is at $1543\text{-}1545\text{ cm}^{-1}$, whereas the adsorbed pyridine is on Lewis acid sites at $1452\text{-}1458\text{ cm}^{-1}$ [14]. It should be pointed out that in case of $\text{Ni}/\text{ZnBr}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts, two peaks appeared corresponding to Lewis acidity, i.e., the peaks at 1452 and 1458 cm^{-1} (Fig. 3)

Catalytic activity

Results obtained with different catalysts are listed in Table 2. Under the experimental condition used (1 atm, $90\text{ }^\circ\text{C}$), $\text{ZnBr}_2/\gamma\text{-Al}_2\text{O}_3$, which carried out under N_2 , (+)-citronellal is converted only to the isopulegol stereoisomer in all range of conversion investigated (entry 1-2). No other reaction products were detected.

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

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

On the acidified supports, the only reaction products were isopulegols due the lack of hydrogenation sites.

A further step of reaction was continued by using the Ni/γ-Al₂O₃ catalysts to hydrogenation of the C=C bonds (entry 3-5). Reaction mixture product of isopulegol isomers firstly separated from residue of ZnBr₂/γ-Al₂O₃ catalyst and changed by Ni/γ-Al₂O₃ catalysts. Next reaction carried out under H₂. The best product as function of hydrogenation C=C bonds on isopulegol obtained in very mild condition (1 atm, 90 °C) with the menthol toward 86.77%.

In contrast, when Ni/γ-Al₂O₃ catalysts used are only slightly active for the isomerisation of (+)-citronellal when reaction carried out under N₂, (yield only 28.24%) (entry 6). The presence of H₂ leads only slightly 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 H₂. Reaction carried out under H₂ 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 H₂ 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 citronellool, **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 those only carbon-carbon double bonds conjugated with a carbonyl group are easily hydrogenated even in the presence of isolated double bonds. Best activities 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 stereoselective isomerisation and hydrogenation sites (entry 10-12). The results obtained have shown that bifunctional catalyst Ni/ZnBr₂/γ-Al₂O₃ 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 ZnBr₂ and Ni supported catalysts. On more acid catalysts, ZnBr₂/γ-Al₂O₃ and Ni/ZnBr₂/γ-Al₂O₃, isopulegols are preferentially formed as primary products. A Ni/γ-Al₂O₃ has shown to be an excellent catalyst for the one step hydrogenation of (+)-citronellal under extremely mild

condition. Its use allows producing menthols with fairly good stereoselectivity.

ACKNOWLEDGEMENT

This work is part of the activities at the Laboratory of Chimica Inorganica, Metallorganica e Analitica, Dipartimento "Lamberta Malatesta", (c/o ISTM-CNR), via Venezian 21, Milano, ITALY. The authors gratefully acknowledge DIKTI for financial support through the Sandwich-like 2009 program. Dr. Nicoletta Ravasio, and Dr. Laura is acknowledged for the TEM analysis.

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