Available online at www.sciencedirect.com

ScienceDirect

Journal of Catalysis 243 (2006) 7–13

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Pt/H-beta zeolites as productive bifunctional catalysts for the one-step citronellal-to-menthol conversion

Pascal Mertens [a], Francis Verpoort [b], Andrei-Nicolae Parvulescu [a], Dirk De Vos [a,*]

[a] *Centre for Surface Chemistry and Catalysis, K.U. Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium*
[b] *Department of Inorganic and Physical Chemistry, U. Gent, Krijgslaan 281, 9000 Gent, Belgium*

Received 24 May 2006; revised 19 June 2006; accepted 21 June 2006

Abstract

Pt-loaded H-beta zeolite was identified as a highly active catalyst for the bifunctional transformation of citronellal to menthol, with isopulegol as the intermediate. With a 2 wt% Pt-loaded catalyst, citronellal is fully converted within 12 h, with only 2.5 wt% catalyst with respect to citronellal, and with a citronellal to Pt molar ratio of 2500. 1,4-Dioxane is the best reaction solvent, because it minimizes the unwanted direct hydrogenation of citronellal and promotes its stereoselective cyclization to isopulegol, leading to high menthol yields. The stereoselectivity can be improved moderately by using a Zr-impregnated support and more substantially by performing high-temperature (750 °C) treatment of the calcined and reduced catalyst. This treatment presumably creates extra Lewis acidity on the catalyst and results in 88% stereoselectivity for the desired menthol. Overall, an 85% yield of (–)-menthol was obtained.

Keywords: Bifunctional catalyst; Chemoselective hydrogenation; Pt/H-beta zeolite; Citronellal; Menthol; Citral

1. Introduction

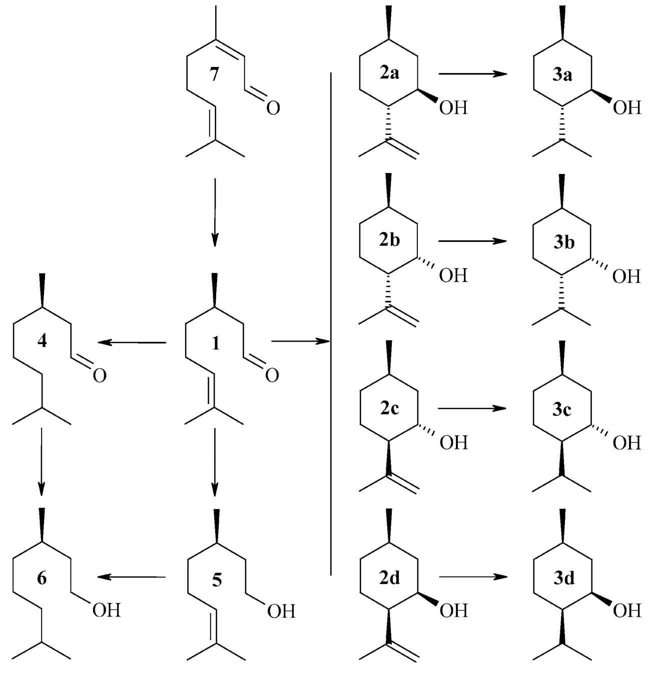
(–)-Menthol is a fine chemical compound often used as a fragrance or flavor in the production of pharmaceuticals, food products, and cosmetics. Established routes for menthol production are multistep processes, such as the Haarmann and Reimer process starting from thymol [1] and the Takasago process starting from myrcene [2]. The synthesis of menthol starting from citronellal comprises two consecutive steps: acid-catalyzed isomerization of citronellal to the cyclic isopulegol intermediate and metal-catalyzed hydrogenation of the double bond in isopulegol, leading to menthol. Along with one stereogenic carbon atom, citronellal (**1**) has two prochiral carbon atoms that are converted to asymmetric centers in the pulegol intermediate (Scheme 1). Consequently, four different pulegol stereoisomers (**2a**–**2d**) can be formed from one citronellal enantiomer. The subsequent hydrogenation results in four different menthol stereoisomers, of which only product **3a**, menthol, is profitable. Less valuable and therefore undesirable isomers are neomenthol (**3b**), isomenthol (**3c**), and neoisomenthol (**3d**).

Transformation of citronellal to menthol in a one-pot process may be an attractive option if a good performing and selective bifunctional catalyst is available. Acid functions on the material should catalyze the cyclization, while a metal function performs the hydrogenation. Previous workers have used Cu as the active metal on a silica support [3] or metallic Ru and ionic Zn immobilized together on SiO_2 [4,5]. Much of this work has focused on obtaining a high summed yield of menthol **3a** and its stereoisomers **3b** and **3c**, or on maximizing the stereoselectivity, that is, the share of the desired isomer **3a** in the total of **3a** + **3b** + **3c**. In practice, hardly any **3d** is formed. In these previous studies, the amount of citronellal converted is quite low, however ($\leqslant 1$ g of substrate per g of catalyst). Similarly low substrate/catalyst ratios were applied in recent work on the one-pot transformation of citral **7** to menthol [6,7]. The latter reaction comprises an additional challenge, because in a supplementary first step, citral needs to be hydrogenated in a chemoselective

---

[*] Corresponding author. Fax: +32 16 32 1998.
E-mail address: dirk.devos@biw.kuleuven.be (D. De Vos).

0021-9517/$ – see front matter
doi:10.1016/j.jcat.2006.06.017



Scheme 1.

way to citronellal. Nickel on mildly acid, Al-containing MCM-41 emerged from these studies as the most promising catalyst, even if decarbonylation of the citral is a nonnegligible side reaction. In any case, citronellal is somewhat less expensive than citral, which makes the reaction starting from citral of limited economic significance.

The present work focuses on identifying highly active and stereoselective catalysts for the citronellal to menthol conversion, with a rapid and selective acid-catalyzed isomerization to isopulegol **2a** followed by a metal-catalyzed hydrogenation to menthol **3a**. Overall, this should result in increased catalyst productivity and menthol stereoselectivity.

2. Experimental

2.1. Catalyst preparation and characterization

Pt/H-beta catalysts were prepared by incipient wetness impregnation of 1 g of calcined, commercial H-beta zeolite (Si/Al = 14, Süd Chemie) with 2 ml of an aqueous K_2PtCl_4 solution. The concentration of the Pt precursor in the impregnation solution depended on the desired metal loading of the zeolite support (1, 2, 3, or 5 wt%). Next, the suspension was dried for 4 h at 90 °C, and the dry powder was successively calcined at 300 °C for 4 h under flowing O_2 (heating rate 2 °C/min; **C300**) and reduced at 350 °C for 6 h under flowing H_2 (heating rate 2 °C/min; **R350**).

In variants of this standard procedure, different H-beta zeolites were used, with Si/Al ratios of 12.5, 14, and 15 (all from Süd Chemie). Alternatively, the standard catalyst preparation was followed by drying at 750 °C in flowing N_2 for 6 h.

For the preparation of 2 wt% Pt/Zr-H-beta catalysts, 0.176 or 0.353 g of $ZrOCl_2 \cdot 8H_2O$ was dissolved in 2 ml of water, and this solution was impregnated on 1 g of H-beta (Si/Al = 14), resulting in 5 or 10 wt% of Zr on the solid. The modified H-beta support was dried for 4 h at 90 °C and then subjected to all further steps of the impregnation with 2 wt% Pt and the standard postsynthesis treatment.

The Pt dispersion (D_{Pt}) was determined by CO chemisorption via titration with 5-µl CO pulses and mass spectrometric detection. Before the measurement, the samples were treated with H_2 at 350 °C, with a heating rate of 1 °C/min; afterwards, the samples were cooled to room temperature and maintained there under He atmosphere. By determining the amount of chemisorbed CO, and assuming an adsorption of 1 CO molecule per accessible Pt atom, D_{Pt} values were obtained. The size of the Pt particles, $d_{Pt,C}$, was derived from the Pt dispersion with the assumption of a cubic Pt particle shape according to White [8]: $d_{Pt,C} = 0.821(1/D_{Pt})$ (nm).

For TEM characterization, the samples were mounted on a copper grid-supported carbon film by depositing droplets of an ultrasonically dispersed suspension of the powder catalyst in ethanol on the grid, with subsequent drying at ambient conditions. The TEM images were recorded on a Philips CM20 electron microscope operating at 200 kV. The average size of the Pt particles, $d_{Pt,T}$, was obtained by calculating the number average diameter for an ensemble of 50 Pt particles observed in TEM.

Pt presence represents the molar amount of Pt on 1 g of the Pt/H-beta catalyst, whereas Pt availability represents the molar amount of accessible surface Pt on 1 g of Pt/H-beta catalyst. The Pt availability was calculated by multiplying the Pt presence value by the dispersion of the Pt/H-beta catalyst.

2.2. Catalytic experiments and analysis

A standard reaction mixture contained 0.6 ml of solvent, 0.4 ml of citronellal, and 0.01 g of the bifunctional powder catalyst. The stirred mixture was then pressurized to 2.0 MPa H_2 and heated to 80 °C. All reactions were performed in a multireactor with 10 minireactors (4 ml volume) from TOP Industries. The pressure in all vessels was kept constant by a continuous supply of reagent gas. Samples were analyzed by gas chromatography (CP-Wax 58 column, flame ionization detector), and retention times were compared with those of commercial reference compounds.

The selectivity to menthols ($S_{menthols}$) is the fraction of menthol and its stereoisomers (**3**) in the sum of all reaction products in the reaction mixture. A low value of $S_{menthols}$ corresponds to a high proportion of 3,7-dimethyl-1-octanol (**6**), pulegols (**2**), etc. in the total of reaction products. The isomer stereoselectivity (S_{stereo}) is the portion of menthol (**3a**) in the pool of menthol stereoisomers (**3**). $\text{Yield}_{menthol}$ is the yield of **3a**, and $\text{Yield}_{menthols}$ is the summed yield of **3a** + **3b** + **3c**.

3. Results and discussion

Although the isomerization of citronellal to isopulegol has often been conducted on a soluble Lewis acid such as Zn^{2+}, Sc^{3+}, or Al^{3+} [9–11], it is clear that the reaction proceeds at equally high rates on H-beta zeolite, which may contain both

Brönsted and Lewis acid sites. Compared with H-beta, using a different acid molecular sieve, like H-mordenite, H-MCM-22, or H-MCM-41, results in substantial side product formation [12]. In previous work, we combined H-beta with metallic Ir for hydrogenation [13]. Because Pt is generally a more active and selective catalyst for C=C hydrogenation than Ir, one may wonder whether conditions can be found in which Pt/H-beta selectively transforms citronellal to menthol. Other metals like Ni and Pd also may be suitable for hydrogenation of the double bond in isopulegol, but their preference for C=C hydrogenation is so high that in practice it is difficult to avoid the direct hydrogenation of citronellal to saturated, noncyclized compounds such as **6**. In attempts to obtain high catalyst productivity coupled with high menthol stereoselectivity, significant variables may include the method of catalyst preparation, the Pt content of the catalyst, the reaction solvent, the H_2 pressure, the reaction temperature, time, and others. Because these variables clearly form a multivariable space, we decided to use a high-throughput catalytic reactor, with 10 parallel reaction positions, to determine the optimal catalyst composition and operation conditions.

3.1. *Transformation of citronellal under inert N_2 atmosphere*

First, the citronellal cyclization to the isopulegol intermediate was examined using various Pt/H-beta catalysts, in the absence of H_2 (Table 1). Particularly in nonpolar solvents, isomerization proceeded smoothly. An extensive solvent screening indicated that 1,4-dioxane is an excellent alternative for cyclohexane, which has been used in previous work for the reaction of citronellal to menthol [13]. Table 1 also shows that the isomerization activity of the catalyst increased with Pt loading (Table 1, entries 3–6). Catalyst pretreatment had a relatively minor effect on isomerization activity; for instance, practically identical results are obtained when catalysts are not reduced or are reduced at 150 or 300 °C (data not shown).

In these isomerization experiments in cyclohexane or 1,4-dioxane, only cyclization products were formed from citronellal. The main products were the desired isopulegol (**2a**) and its stereoisomers neoisopulegol (**2b**) and isoisopulegol (**2c**), together with minor amounts of menthols. Typically, the fraction of isopulegol **2a** in the total of pulegol isomers (**2a** + **2b** + **2c**) amounted to 75%. Because some menthols were found in reactions under N_2 over Pt catalysts but not in the reaction with H-beta as such, it seems that solvent dehydrogenation provided chemisorbed hydrogen on the Pt surface. This hydrogen was then used, in a hydrogen transfer reaction, for reduction of pulegols to the corresponding menthols. Careful chromatographic analysis showed that in the reaction of citronellal over Pt/H-beta under 2.0 MPa N_2 atmosphere in cyclohexane, a small amount of cyclohexene was indeed formed. This hydrogen transfer reaction was so slow that no products of direct C=C or C=O hydrogenation of citronellal were formed; the cyclization clearly preceded the reduction reaction. As can be expected, the isomer distribution in the pulegols determined the ratio of the different menthols, resulting in a selectivity for menthol **3a** ($S_{\text{stereo}} = \mathbf{3a}/(\mathbf{3a} + \mathbf{3b} + \mathbf{3c})$) of around 75%.

3.2. *Transformation of citronellal under H_2 atmosphere*

Preliminary experiments on citronellal transformation under H_2 atmosphere over Pt/H-beta showed that besides pulegol (**2**) and menthol (**3**) isomers, only 3,7-dimethyl-1-octanol (**6**) was eventually obtained in significant amounts as a byproduct. In the direct hydrogenation of citronellal over Pt/H-beta, initially citronellol (**5**) rather than 3,7-dimethyloctanal (**4**) was formed. This reflects that the trisubstituted double bond in citronellal was hydrogenated relatively slowly; for rapid hydrogenation of sterically hindered double bonds on Pt, often a liquid acid (e.g., CH_3COOH or $HClO_4$) must be added to the reaction solvent [14]. Subsequently, citronellol was converted into 3,7-dimethyl-1-octanol. Thus the selectivity was determined by the competition between the ene reaction (**1** → **2**) and the direct hydrogenation of citronellal (**1** → **4**, **5**, **6**). Obviously, the reduction was much faster under H_2 atmosphere than under N_2, and products of solvent dehydrogenation were not observed.

3.2.1. *Effect of solvent*

The most important factor influencing the reaction selectivity is the solvent applied. Therefore, a broad solvent screening was performed using 2 wt% Pt/H-beta, considering both polar and nonpolar solvents (Table 2, entries 1–5). In 1,4-dioxane, formation of 3,7-dimethyloctanol was minimal, and the highest menthol yields were obtained. The advantage of using 1,4-dioxane instead of aliphatic or aromatic hydrocarbon solvents was quite significant. Polar solvents, such as alcohols, resulted in relatively high selectivities for products of direct hydrogenation of citronellal. It is indeed known that alcohols are preferred solvents for the hydrogenation of aldehydes on platinum group metals [14]. In addition, alcohol solvents cause formation of

Table 1
Yield of pulegols (**2**) and menthols (**3**) from citronellal (**1**) under N_2 atmosphere

No.	Catalyst	Solvent	$\text{Conversion}_{\text{citronellal}}$ (%)		$\text{Yield}_{\text{pulegols}}$ (%)		$\text{Yield}_{\text{menthols}}$ (%)	
			at 40 °C	at 80 °C	at 40 °C	at 80 °C	at 40 °C	at 80 °C
1	2% Pt/H-beta	Cyclohexane	90.2	94.2	89.8	92.9	0.4	1.3
2	2% Pt/H-beta	1,4-Dioxane	94.9	98.7	94.4	96.8	0.5	1.9
3	H-beta	1,4-Dioxane	66.8	74.5	66.8	74.5	0.0	0.0
4	1% Pt/H-beta	1,4-Dioxane	82.3	91.1	82.2	90.4	0.1	0.7
5	2% Pt/H-beta	1,4-Dioxane	95.1	98.8	94.5	97.2	0.6	1.6
6	3% Pt/H-beta	1,4-Dioxane	97.9	99.9	96.5	98.1	1.4	1.8

Reaction conditions: 0.4 g citronellal, 0.01 g catalyst, 1 ml solvent, 2.0 MPa N_2, 6 h.

Table 2
Effect of solvent and Pt loading on the citronellal (**1**) transformation to menthol (**3a**)

No.	Catalyst	Solvent	Yield$_{3,7\text{-dimethyloctanol}}$ (%)	Yield$_{\text{pulegols}}$ (%)	Yield$_{\text{menthols}}$ (%)	Yield$_{\text{menthol}}$ (%)	S_{stereo} (%)
1	2% Pt/H-beta	Tetrahydrofuran	44.6	14.1	41.3	31.1	75.4
2	2% Pt/H-beta	Toluene	39.8	6.4	53.8	39.4	73.2
3	2% Pt/H-beta	*para*-Xylene	34.7	9.8	55.5	40.3	72.6
4	2% Pt/H-beta	Cyclohexane	22.9	5.4	71.7	54.6	76.2
5	2% Pt/H-beta	1,4-Dioxane	5.1	2.1	92.8	70.5	76.0
6	1% Pt/H-beta	1,4-Dioxane	2.7	16.7	80.6	61.3	76.0
7	2% Pt/H-beta	1,4-Dioxane	4.6	2.0	93.4	71.3	76.3
8	3% Pt/H-beta	1,4-Dioxane	16.9	5.8	77.3	59.2	76.6
9	5% Pt/H-beta	1,4-Dioxane	39.7	6.4	53.9	40.9	75.9

Reaction conditions: 0.4 g citronellal, 0.01 g catalyst, 1 ml solvent, 80 °C, 2.0 MPa H_2, conversion >99%, 12 h.

Table 3
Effect of temperature and H_2 pressure on the citronellal (**1**) transformation

No.	Temperature (°C)	H_2 pressure (MPa)	Yield$_{3,7\text{-dimethyloctanol}}$ (%)	Yield$_{\text{pulegols}}$ (%)	Yield$_{\text{menthols}}$ (%)	Yield$_{\text{menthol}}$ (%)
1	25	2.0	2.3	16.9	80.8	61.2
2	50	2.0	3.8	11.8	84.4	64.6
3	75	2.0	4.2	3.4	92.4	69.5
4	100	2.0	4.9	2.2	92.9	70.6
5	80	0.2	0.4	5.8	93.8	70.7
6	80	0.5	1.9	4.7	93.4	70.8
7	80	1.0	2.8	4.3	92.9	70.0
8	80	2.0	4.4	2.9	92.7	69.7

Reaction conditions: 0.4 g citronellal, 0.01 g 2% Pt/H-beta, 1 ml 1,4-dioxane, conversion >99%, 12 h.

Table 4
Comparison between two reaction procedures in the transformation of citronellal (**1**)

No.	Procedure	Solvent	Yield$_{3,7\text{-dimethyloctanol}}$ (%)	Yield$_{\text{pulegols}}$ (%)	Yield$_{\text{menthols}}$ (%)	Yield$_{\text{menthol}}$ (%)	S_{stereo} (%)
1	1	Cyclohexane	0.0	1.6	98.4	76.1	77.3
2	1	1,4-Dioxane	0.0	2.9	97.1	75.9	78.2
3	2	Cyclohexane	23.2	4.6	72.2	55.3	76.6
4	2	1,4-Dioxane	4.2	2.2	93.6	72.2	77.1

Reaction conditions: procedure 1: 6 h 2.0 MPa N_2, 12 h 2.0 MPa H_2; procedure 2: 12 h 2.0 MPa H_2; 0.4 g citronellal, 0.01 g 2% Pt/H-beta catalyst, 1 ml solvent, 80 °C, conversion >99%.

such side products as (hemi-)acetals, especially when small primary alcohols are used as solvents in the presence of acid catalysts. But not all cyclic ethers are equally good solvents, as demonstrated by the low yield of menthols in tetrahydrofuran (entry 1). Polarity does not seem to be the key variable affecting the selectivity, because cyclohexane and 1,4-dioxane have similar dielectric constants, ε; however, these solvents' hydrogen bond-accepting properties are obviously different.

3.2.2. *Effect of Pt loading*

After selection of an optimal solvent, Pt loading is the next most significant variable. As shown in Table 1, Pt not only functions as a reduction catalyst; but also accelerates cyclization. Therefore, Pt content should be optimized to provide the proper relative rates of both sequential reactions (Table 2, entries 6–9). Raising the Pt loading above 2 wt% resulted in too much direct citronellal hydrogenation, with 3,7-dimethyl-1-octanol yields exceeding 15%. This can be avoided using 1 wt% Pt/H-beta; but in this case, the hydrogenation of the pulegol isomers was not yet complete after 12 h. Therefore, 2 wt% Pt/H-beta seems to be an optimal loading. Although this Pt loading might seem relatively high, note that only 2.5 wt% catalyst was used, corresponding to an effective citronellal:Pt molar ratio of 2500:1.

3.2.3. *Effect of temperature and H_2 pressure*

Variation of the reaction temperature shows that at least 75 °C was required for a sufficient hydrogenation rate of the pulegol isomers; at lower temperatures, a sizable amount of pulegols was recovered after 12 h of reaction (Table 3, entries 1–4). A temperature increase not only raised the menthol yields, but also produced a small, but significant, increase in the amount of direct citronellal hydrogenation, from 2.3% at 25 °C to 4.9% at 100 °C. These observations suggest that the Pt-catalyzed hydrogenation of either citronellal or isopulegols had greater apparent activation energy than cyclization. Selectivity differences between reactions at 75 and 100 °C were marginal (Table 4, entries 3 and 4). Although an optimal hydrogen pressure might also be expected, the effects of pressure on the menthol isomer yield was small; very little direct hydrogenation was observed at 0.2 MPa H_2, but this effect was balanced by the less effective hydrogenation of pulegols at this pressure.

3.2.4. Comparison of reaction procedures

To maximize the citronellal transformation to menthol, two different reaction procedures were compared. In procedure 1, the reaction was conducted for 6 h under N_2 atmosphere and subsequently for 12 h under H_2; alternatively, in procedure 2, the H_2 atmosphere was maintained for the full reaction duration of 12 h. The first procedure yielded 97–98% of menthol isomers whether performed in 1,4-dioxane or in cyclohexane. This corresponds to menthol yields of >75% (Table 4, entries 1 and 2). Clearly, the absence of H_2 prevents the unfavorable initial hydrogenation of citronellal normally observed in cyclohexane (Table 4, entry 3). In comparison, the best yield of menthol **3a** under continuous H_2 pressure and using the standard 2 wt% Pt/H-beta catalyst was 72% (Table 4, entry 4).

3.2.5. Modification of reaction stereoselectivity

Given the very high yields of menthol isomers from citronellal, and with a highly productive catalyst in hand, the only aspect to be improved is the stereoselectivity to **2a** in cyclization, which eventually determines the stereoselectivity for **3a**. Two approaches were followed. First, Zr was deposited on the beta zeolite before introduction of the Pt [15,16]; second, the catalyst was subjected to an extra pretreatment at high temperature [17]. Introduction of additional Lewis acid atoms in the structure was recently proven successful by Corma and Renz [18], who reported a 85% stereoselectivity to isopulegol over a Sn-substituted beta zeolite. With the Zr-loaded Pt/H-beta catalyst, only modest increases in stereoselectivity were obtained, for example, from 78 to 80% for a sample loaded with 5 wt% Zr and a Si/Al ratio of 14 (Table 5, entries 1–3). More substantial improvements were realized by heating the calcined and reduced catalyst to 750 °C. This treatment probably converts part of the Brönsted sites to Lewis sites [17], which may affect the isopulegol:neoisopulegol:isoisopulegol (**2a**:**2b**:**2c**) ratio in the cyclization. After this treatment, the H-beta zeolite with Si/Al ratio 14 emerged as the most appropriate isomerization catalyst, with a S_{stereo} of 88.0%, in comparison to the 78.9% obtained with the catalyst as such (Table 5, entry 7). For other H-beta catalysts from several batches, with slightly different Si/Al ratios, high-temperature treatment also proved beneficial to increasing the stereoselectivity and menthol yield (Table 5, entries 5 and 9).

3.3. Transformation of citral under H_2 atmosphere

In a final series of experiments, the optimized 2 wt% Pt/H-beta catalyst was applied in menthol synthesis starting from citral. Table 6 shows that in identical conditions, the S_{menthols} was considerably lower starting from citral than from citronellal (entries 1 and 2). In this three-step menthol formation, citral should initially be converted to citronellal. Along with citronellal, the doubly unsaturated alcohol isomers geraniol and nerol were also formed initially; 3,7-dimethyl-2-octenal was not observed. The competition between these initial hydrogenation steps partially accounts for the lower chemoselectivity compared with the menthol synthesis starting from citronellal. Moreover, both citronellal and geraniol or nerol can be consecutively hydrogenated, and, as before, this direct citronellal hydrogenation to citronellol instead of its cyclization to isopulegol was an additional cause of chemoselectivity loss. Again, only 3,7-dimethyl-1-octanol was observed as a cyclic hydrogenation product at the end of the reaction. Ni and Pd are probably more

Table 5
Menthol (**3a**) yield and stereoselectivity as a function of support pre- and post-treatments

No.	Support	$\text{Yield}_{\text{menthols}}$ (%)	$\text{Yield}_{\text{menthol}}$ (%)	S_{stereo} (%)
1	H-beta (Si/Al ≈ 14)	97.2	76.1	78.3
2	5 wt% Zr/H-beta (Si/Al ≈ 14)	99.5	80.1	80.2
3	10 wt% Zr/H-beta (Si/Al ≈ 14)	99.5	78.8	78.9
4	H-beta (Si/Al = 12, 5)	95.1	71.3	75.0
5	H-beta (Si/Al = 12, 5) 750 °C	95.0	78.2	82.3
6	H-beta (Si/Al = 14)	98.3	77.6	78.9
7	H-beta (Si/Al = 14) 750 °C	96.2	84.7	88.0
8	H-beta (Si/Al = 15)	99.2	74.2	74.8
9	H-beta (Si/Al = 15) 750 °C	98.9	79.8	80.7

Reaction conditions: 0.4 g citronellal, 0.01 g 2% Pt/support, 1 ml 1,4-dioxane, 25 °C, 6 h 2.0 MPa N_2, 12 h 2.0 MPa H_2, conversion >99%.

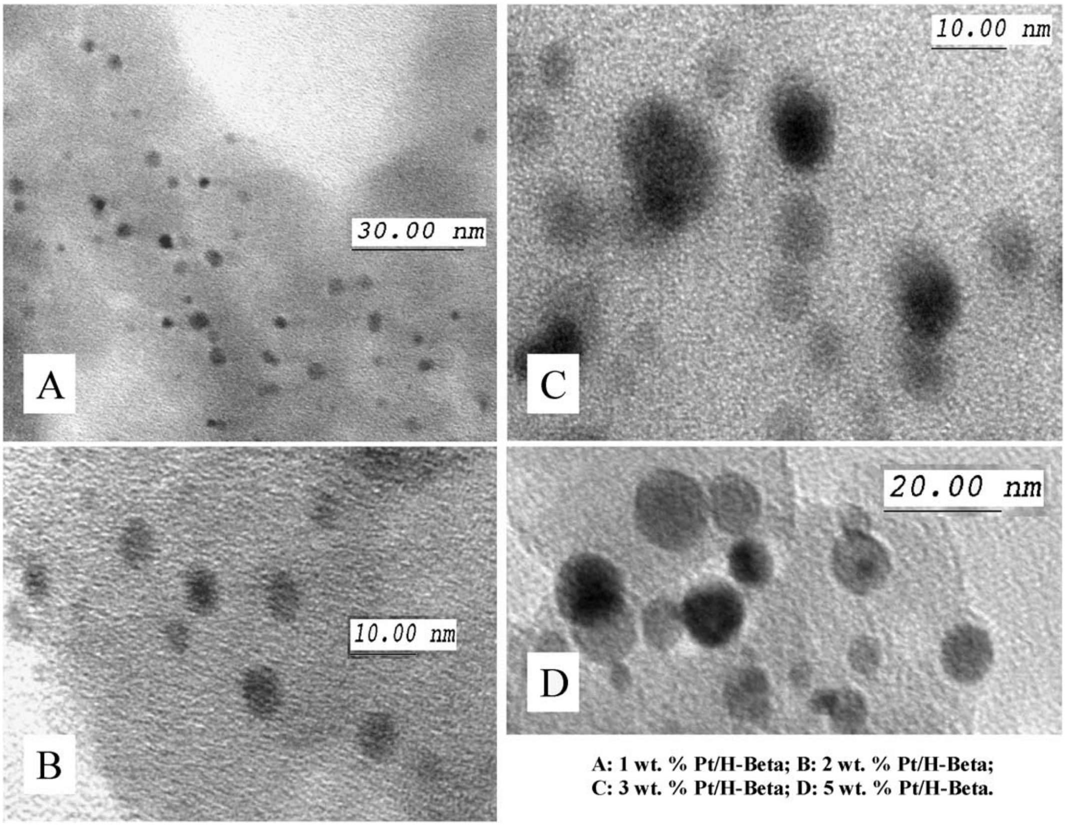
Table 6
Comparison between transformation of citronellal (**1**) and citral (**7**) to menthol (**3a**)

No.	Solvent	Substrate	$\text{Yield}_{3,7\text{-dimethyloctanol}}$ (%)	$\text{Yield}_{\text{pulegols}}$ (%)	$\text{Yield}_{\text{menthols}}$ (%)	$\text{Yield}_{\text{menthol}}$ (%)
1	Cyclohexane	Citronellal	23.8	6.5	69.7	53.3
2	Cyclohexane	Citral	39.8	6.2	54.0	41.0
3	1,4-Dioxane	Citronellal	3.8	2.4	93.8	72.0
4	1,4-Dioxane	Citral	17.7	1.2	81.1	62.5

Reaction conditions: 0.4 g citronellal or citral, 0.01 g 2% Pt/H-beta catalyst, 1 ml solvent, 80 °C, 2.0 MPa H_2, conversion >99%, 12 h.

Table 7
Platinum dispersion, Pt particle size and Pt availability of the various Pt/H-beta catalysts

No.	Pt loading (wt%)	D_{Pt} (%)	$d_{\mathrm{Pt,C}}$ (nm)	$d_{\mathrm{Pt,T}}$ (nm)	Pt presence (10^{-6} mol/g)	Pt availability (10^{-6} mol/g)
1	1	12.25	6.7	4.9	51.3	6.3
2	2	7.25	11.3	6.7	102.5	7.5
3	3	5.95	13.8	8.5	153.8	9.2
4	5	5.56	14.8	12.0	256.3	14.2



A: 1 wt. % Pt/H-Beta; B: 2 wt. % Pt/H-Beta;
C: 3 wt. % Pt/H-Beta; D: 5 wt. % Pt/H-Beta.

Fig. 1. Transmission electron micrographs of the various Pt/H-Beta catalysts.

appropriate for menthol synthesis starting from citral, because they reduce more selectively the C=C bonds, which can result in improved production of the citronellal intermediate [6].

3.4. Characterization of Pt/H-beta catalysts

Table 7 reports the values of D_{Pt} for the standard Pt/H-beta catalysts. A decline in Pt dispersion was observed for catalysts with higher Pt loadings. For the 2 wt% Pt/H-beta, 7.25% of the Pt atoms present was accessible. Based on the Pt dispersion, the size of the Pt particles was calculated, and these $d_{\mathrm{Pt,C}}$ values were compared with the $d_{\mathrm{Pt,T}}$ values from the TEM characterization. TEM pictures of the Pt/H-beta catalysts with varying loading are reproduced in Fig. 1. A similar trend of increased Pt particle size at higher Pt loadings was obtained via both techniques for particle diameter determination, as reflected in Table 7. Because the $d_{\mathrm{Pt,T}}$ value was substantially lower than the $d_{\mathrm{Pt,C}}$ value, it seems that a fraction of the Pt surface atoms remained inaccessible or poisoned (by, e.g., chloride species), even after the standard postsynthesis treatment. For the 2 wt% Pt/H-beta, a $d_{\mathrm{Pt,T}}$ value of 6.7 nm was determined. TEM characterization of a 2 wt% Pt/H-beta that had also been subjected to the high-temperature treatment found that the $d_{\mathrm{Pt,T}}$ was not affected, indicating that this postsynthesis treatment does not affect the Pt particles. Moreover, calculations of Pt availability for the Pt/H-beta catalysts (Table 7) show that a 5 times higher Pt loading led to only a doubling of Pt availability. The relatively low D_{Pt} value for the 5 wt% Pt/H-beta catalyst was due to the larger diameters of the individual particles and also to a more pronounced aggregation of the particles on the outer surface of the zeolite, as shown in Fig. 1d.

4. General discussion

The bifunctional Pt/H-beta zeolite has proven to be an efficient and highly selective catalyst for menthol synthesis from citronellal, especially in 1,4-dioxane and with a Pt loading of 2 wt%. Selectivities to menthols exceeding 95% were achievable in the one-step transformation, combined with yields of the desired menthol up to 76%.

Several factors seem to be essential in obtaining this result. First, the Pt discriminates quite well between disubstituted C=C double bonds, as in pulegols, and trisubstituted bonds, as in citronellal, which are only slowly hydrogenated. This is reminiscent of, for example, the chemoselective hydrogenation of limonene on Pt/C, in which only the exocyclic disubstituted bond reacts [14]. A metal like Pd is much less suitable for realizing such chemoselectivity, because Pd facilitates double-bond isomerization. Because the C=C bond in citronellal is hardly hydrogenated on a 2 wt% Pt catalyst, there is sufficient time for the ene-like cyclization to proceed. The pulegol isomerization products **2a** → **2d** have a disubstituted double bond and are much more prone to hydrogenation, leading eventually to the desired menthol isomers **3**.

Second, the catalyst also discriminates well between C=C hydrogenation in the pulegols and the undesired C=O hydrogenation in citronellal. This is essential to avoid citronellol formation from citronellal. Indeed, Pt is known to be a suitable catalyst for C=O hydrogenation only when specific compounds, such as Fe^{3+} or Sn^{4+}, are used in the support material or as a promotor [14,19]. Only when using the 5 wt% Pt catalyst was an unexpectedly pronounced C=O hydrogenation observed (Table 2, entry 9). Although this can be due in part to the relative amounts of acid and hydrogenating functions, one should also consider that the 5 wt% catalyst contains the largest and most aggregated Pt particles. This seems to indicate that large particles more readily hydrogenate the C=O bonds. A similar enhanced selectivity for C=O hydrogenation on large Pt metal particles (>6 nm) with flat surfaces in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol has been reported by Gallezot et al. [20]. For the Pt/H-beta catalysts with lower Pt content and smaller particle size, direct C=O hydrogenation can be limited, which directs the overall reaction toward cyclic products.

Third, choosing appropriate solvents helps obtain high selectivities. For instance, alcohols are less suitable because they are the typical solvents for selective C=O reduction in the presence of C=C bonds. In 1,4-dioxane, the rates of the consecutive reactions seem well tuned to give high menthol yields.

Finally, a further stereoselectivity increase was obtained after high-temperature treatment of the bifunctional beta catalyst under inert atmosphere. There is ample spectroscopic and physicochemical evidence to indicate that high-temperature treatment of beta zeolites, possibly in combination with steam, converts pseudotetrahedral or pseudooctohedral species [e.g., $(H_2O)Al(OSi)_3$ or $(H_2O)_3Al(OSi)_3$] to framework Lewis acid sites [e.g., $Al(OSi)_3$ or $Al(OSi)_2OH$] [21–23]. Temperatures well above 450 °C seem to be required for this process. Because the Lewis acid site is embedded in the pore wall, it may display unusual stereoselectivity. This has been well documented for the Meerwein reduction of 4-t-butylcyclohexanone in zeolite beta [23]; similar effects may be invoked here to explain the increased stereoselectivity to isopulegol **2a**. The postsynthesis catalyst treatment eventually resulted in a menthol stereoselectivity of 88% and a menthol yield of 85%.

Acknowledgments

P.M. thanks the IWT for financial support. This work was performed in the frame of the Belgian Interuniversity Poles of Attraction (IUAP V-3). D.D.V. is grateful to the FWO for grant G.0323.04. The authors thank Xingpu Ye for assistance with the TEM characterization of the catalysts.

References

[1] J. Fleischer, K. Bauer, R. Hopp, DE 2109456, Haarmann & Reimer, 1971.

[2] S. Otsuka, K. Tani, T. Yamagata, S. Akutagawa, H. Kumobayashi, M. Yagi, EP 68506, Takasago, 1972.

[3] N. Ravasio, N. Poli, R. Psaro, M. Saba, F. Zaccheria, Top. Catal. 213 (2000) 195.

[4] C. Milone, C. Gangemi, R. Ingoglia, G. Neri, S. Galvagno, Appl. Catal. A 184 (1999) 89.

[5] C. Milone, C. Gangemi, G. Neri, A. Pistone, S. Galvagno, Appl. Catal. A 199 (2000) 239.

[6] A.F. Trasarti, A.J. Marchi, C.R. Apesteguia, J. Catal. 224 (2004) 484.

[7] P. Mäki-Arvela, N. Kumar, D. Kubicka, A. Nasir, T. Heikkilä, V.-P. Lehto, R. Sjöholm, T. Salmi, D.Yu. Murzin, J. Mol. Catal. A 240 (2005) 72.

[8] M.G. White, Heterogeneous Catalysis, Prentice–Hall, Englewood Cliffs, NJ, 1991, 88.

[9] Y. Nakatani, K. Kawashima, Synthesis (1978) 147.

[10] V.K. Aggarwal, G.P. Vennall, P.N. Davey, C. Newman, Tetrahedron Lett. 39 (1998).

[11] T. Iwata, Y. Okeda, Y. Hori, Eur. Pat. Appl. EP 12251632 A2, 2002.

[12] P. Maki-Arvela, N. Kumar, V. Nieminen, R. Sjöholm, T. Salmi, D.Yu. Murzin, J. Catal. 225 (2004) 155.

[13] F. Iosif, S. Coman, V. Pârvulescu, P. Grange, S. Delsarte, D. De Vos, P. Jacobs, Chem. Commun. (2004) 1292.

[14] S. Nishimura, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, Wiley, New York, 2001.

[15] G.K. Chuach, S.H. Liu, S. Jaenicke, L.J. Harrison, J. Catal. 200 (2001) 352.

[16] Z. Yongzhong, N. Yuntong, S. Jaenicke, G.K. Chuach, J. Catal. 229 (2005) 404.

[17] T.A. Peters, N.E. Benes, A. Holmen, J.T.F. Keurentjes, Appl. Catal. A 297 (2006) 182.

[18] A. Corma, M. Renz, Chem. Commun. (2004) 550.

[19] V. Ponec, Appl. Catal. A 149 (1997) 27.

[20] A. Giroir-Fendler, D. Richard, P. Gallezot, Catal. Lett. 5 (1990) 175.

[21] G.H. Kuehl, H.K.C. Timken, Micropor. Mesopor. Mater. 35–36 (2000) 521.

[22] J.A. van Bokhoven, D.C. Koningsberger, P. Kunkeler, H. van Bekkum, J. Catal. 211 (2002) 540.

[23] P.J. Kunkeler, B.J. Zuurdeeg, J.C. van der Waal, J.A. van Bokhoven, D.C. Koningsberger, H. van Bekkum, J. Catal. 180 (1998) 234.