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# Highly selective menthol synthesis by one-pot transformation of citronellal using Ru/H-BEA catalysts



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#### 1. Introduction

With an annual production of about 20,000 tons (2007), menthol is one of the world's most common aroma compounds [1]. It is used in pharmaceuticals, toothpastes, and tobacco, with secondary applications in chewing gum, cosmetics, and confectionery [1,2]. Natural menthol, which accounts for more than half of the whole menthol production, is extracted from Mentha arvensis or Mentha piperita in India, China, Japan, Brazil, and Taiwan [2]. Because of its three chiral centers in the cyclohexane ring, menthol has four stereoisomeric pairs (Fig. 1). But only (-)-menthol has the typical strong odor and the characteristic cooling effect [1]. Consequently, the other stereoisomers (±)-neo-menthol, (±)-iso-menthol and (±)-neoiso-menthol as well as (+)-menthol are less valuable and undesired. While natural menthol exists as the pure (-)-menthol [1], for synthetic menthol, it is either necessary to treat the racemic menthol in a separation crystallization process (Haarmann-Reimer process) or to use a chiral homogeneous catalyst (Takasago and BASF process) [2,3].

Due to the disadvantages of homogenous catalysts such as separation and the high prices for the homogenous metal complexes, the use of heterogeneous catalysts can be a more attractive alternative. A promising route to produce menthol with heterogeneous

## ABSTRACT

The one-pot transformation of citronellal to menthol requires a combined cyclization-hydrogenation step for which Ru/H-BEA catalysts were identified as highly active and selective catalysts. After identifying zeolite H-BEA as the most promising heterogeneous catalyst for the cyclization of citronellal to the intermediate isopulegol, bifunctional metal/H-BEA catalysts were investigated in the one-pot transformation of citronellal to menthols. Using Pd undesired defunctionalization prevailed, while using Pt and Ru, the formation of menthols predominated. Finally, for Ru/H-BEA catalysts, the effect of catalyst composition (Si:Al ratio, Ru content) and reaction conditions (temperature, hydrogen pressure, and solvent) was investigated to diminish citronellal hydrogenation, dimerization, and defunctionalization. Accordingly, with a 1%Ru/H-BEA-25 catalyst (Ru particle size = 1 nm) in dioxane at 15 bar hydrogen pressure and 373 K, a very high selectivity to menthols of 93% at nearly full conversion was obtained. The catalyst is also highly diastereoselective producing 79% of the desired (±)-menthol.

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catalysts is the one-pot transformation of citronellal to menthol (Fig. 1). This reaction involves two crucial steps: the cyclization of citronellal to isopulegols (ISPs; route 1) and the hydrogenation of the obtained isopulegols to menthols (MTs; route 2). Note that using racemic citronellal as reactant, only racemic menthols (and isopulegols) can be obtained.

Due to the existence of the four enantiomeric pairs of isopulegol and menthol, it is necessary to avoid the formation of the non-valuable isomers. Furthermore, the following reactions should be avoided: hydrogenation of citronellal (route 3), dimerization of citronellal via aldol condensation (Fig. 1, route 4b), dimerization of isopulegol to di-isopulegol ethers (route 4c), and the defunctionalization of isopulegols to p-menthadienes, p-menthenes, and p-menthanes (route 4a).

For the cyclization of citronellal, several Lewis and Brønstedt acids were investigated in prior studies, for example supported or non-supported Lewis acids such as  $ZnBr_2$ ,  $ZnCl_2$ ,  $FeSO_4$  [4–6], supported or non-supported heteropoly acids [7,8] sulfated or phosphated zirconia [9,10],  $ZrO_2$  dispersed in SiO<sub>2</sub> – montmorillonite [11] and zeolites [9,12–15]. Very high isopulegol yields were achieved with most catalysts, but the distribution of the four isopulegol diastereomers differed strongly. In all cases, the desired stereoisomer (±)-isopulegol was obtained as the predominant isomer. But using solid acids such as zeolites, fractions of (±)-isopulegol of about 70–75% [9,13,14] were obtained, which represents the thermodynamic equilibrium [13]. Higher (±)-isopulegol





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fractions of >90% were obtained with Lewis acids such as ZnBr<sub>2</sub> [2,6], Sn-BEA [15], or Zr-BEA [14].

For the one-pot transformation of citronellal to menthols, several bifunctional metal/solid acid catalysts and silica-supported bifunctional systems have been investigated.

For example, using Ru/ZnBr<sub>2</sub>/SiO<sub>2</sub> [16], Pt/Ga/MCM-4 [17], or Pd/H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> [18], menthol yields of around 90% were obtained, and with a physical mixture of  $ZnBr_2/Al_2O_3$  and Ni/Al<sub>2</sub>O<sub>3</sub>, a yield of 75% was reached [19]. Furthermore, bifunctional metal organic frameworks (MOFs; Pd@MIL-101) converted citronellal with a yield of 86% [20].

The highest menthol selectivities of around 93% were obtained with metal/zeolite catalysts, for example, Ni/Zr-BEA [21], Pt/H-BEA [22], and Ir/H-BEA [23,24].

Using the metals Pt and Ir, conditions such as loading of the active metal, temperature, pressure, and solvent had an enormous

effect on the obtained product distribution. While in both cases, the influence of loading, temperature, and pressure shows the same dependencies (a low hydrogen pressure, a low loading, and a temperature of 353–373 K lead to high menthol selectivities), the solvent shows different dependencies. While using Ir/H-BEA nonpolar solvents as cyclohexane improves the selectivity to menthols [24], using Pt/H-BEA polar aprotic solvents as dioxane leads to high menthol selectivities [22].

The present work systematically investigates the first step of menthol synthesis, i.e. the cyclization of citronellal, where H-BEA was identified as useful catalyst, and then the one-pot transformation of citronellal to menthols on bifunctional metal (Pd, Pt, and Ru)/H-BEA catalysts. Characterization was carried out by means of CO chemisorption and temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD). Using Ru/H-BEA, whose ability for the title reaction is unknown so far, the influence of the Si:Al ratio as well



Fig. 1. Reaction network of the transformation of citronellal to menthol. Note that the name *menthols* involves the group of the menthol stereoisomers, whereas *menthol* is used for enantiomeric menthol pair. Only one enantiomer is shown in each case.

as Ru loading, reaction temperature, hydrogen pressure, and solvent should be understood to obtain an optimized catalyst system for the selective transformation of citronellal to menthol.

#### 2. Experimental

### 2.1. Catalyst preparation

Sulfated zirconia (ZrO<sub>2</sub>-SO<sub>4</sub>) was synthesized by sol-gel method [25]. To a solution of zirconium i-propoxide (70 wt% in 1-propanol, Sigma–Aldrich) and 2-propanol (70 wt% in 1-propanol, Sigma–Aldrich) sulfuric acid (95.0–98.0 wt%, Sigma–Aldrich) was added dropwise and stirred for 10 min. Over a period of 2 h, a solution of water and 2-propanol was added and the resulting gel was stirred for an additional hour. The molar ratios were as follows:  $H_2SO_4/Zr = 0.2$ ;  $H_2O/Zr = 13.4$ ; 2-propanol/Zr = 13.2. The gel was dried at room temperature for two days, at 373 K for 12 h and calcined at 823 K in an air flow.

Supported metal catalysts were obtained by incipient-wetness impregnation of different types of zeolite H-BEA (Clariant) as supports using Ru(NO)(NO<sub>3</sub>)<sub>3</sub> (Alfa Aeser), Pd(NO<sub>3</sub>)<sub>2</sub> (Alfa Aeser), or Pt(acac)<sub>2</sub> (ABCR) as metal precursor and water (for Pd and Ru catalysts) or toluene (for the Pt precursor) as solvent. The zeolite materials differ in the Si:Al ratio (25, 35, and 150) and specific surface areas (493, 660, and 595 m<sup>2</sup> g<sup>-1</sup>, respectively). The samples were dried overnight at 373 K. The Pd catalysts were calcined in air flow at 773 K. All catalysts were reduced ex situ in flowing hydrogen (Pd/H-BEA at 723 K, Pt/H-BEA and Ru/H-BEA at 623 K; TPR analysis of the stored catalyst does not indicate an incurring oxidation, not shown here). The metal content of the obtained catalysts was validated via ICP measurements (not shown here).

## 2.2. Catalytic testing

The cyclization experiments were carried out in a 25-mL roundbottomed flask equipped with a reflux condenser using *n*-hexane (Roth) as solvent at 353 K. The flask was charged with 50 mg catalyst, 10 mL *n*-hexane, and 0.1 mL *n*-tetradecane (Merck) as internal GC standard. After reaching the desired temperature, 0.5 mL racemic citronellal (Merck) was added. This was defined as the start of the reaction. After 1 h, the reaction was stopped and the sample was analyzed by gas chromatography (Shimadzu GC 2010 Plus) using an Agilent DB-Wax column (348 K, 5 min; 1 K min<sup>-1</sup>  $\rightarrow$  381 K; 5 K min<sup>-1</sup>  $\rightarrow$  413 K; 20 K min<sup>-1</sup>  $\rightarrow$  493 K, 5 min).

The hydrogenation experiments were carried out in a stainless steel autoclave (Parr 4843, 300 mL) usually using *n*-hexane (Roth) as solvent at 373 K and 25 bar hydrogen pressure. The reactor was charged with 0.5 g catalyst, 150 mL solvent, and 1 mL *n*-tetradecane (Merck) as internal GC standard. After reaching the desired temperature, 4.5 g racemic citronellal (Merck) was added and the reactor was pressurized over a separate tank. This was defined as the start of the reaction. Samples were taken periodically and analyzed by gas chromatography as described above. The reproducibility of the experimental setup and the catalyst preparation was verified by repeating the same experiment with different catalyst charges. The deviation of the calculated menthol concentration was about maximum 4%.

Note that it was ensured by using powdered catalysts (particle size distribution  $d_{90\%}$  of <20 µm) and a stirring rate of 1000 rpm that the reactions were expired under chemical control.

## 2.3. Characterization

## 2.3.1. Temperature-programmed desorption of NH<sub>3</sub>

The amount of acid sites was determined by temperatureprogrammed desorption of NH<sub>3</sub>. After calcination at 673 K, the sample was exposed to NH<sub>3</sub> at 308 K for 1 h. Weakly adsorbed NH<sub>3</sub> was removed by flowing nitrogen at 308 K. Finally, the temperature was increased with a rate of 5 K min<sup>-1</sup> up to 923 K, and the amount of NH<sub>3</sub> was measured by FT-IR spectrometry (Thermo Fischer Scientific).

#### 2.3.2. CO chemisorption

The size of the metal particles was determined by CO chemisorption measurements, which were carried out on an apparatus TPD/R/O 1100 (Thermo Fisher Scientific). Therefore, the quartz reactor was loaded with a sample. After reducing the catalysts at 473 K for 1 h followed by cooling down to 273 K in a hydrogen flow CO pulses with a volume of 0.473 mL were introduced. Assuming an adsorption of one CO molecule per accessible metal atom, the amount of chemisorbed CO was determined and the metal particle size was obtained via  $d = 6(v_m/a_m)D^{-1}$  with  $v_m$  = volume occupied by an atom in bulk metal,  $a_m$  = area occupied by a surface atom and D = dispersion [26]. The obtained particle sizes were validated via TEM measurements (not shown here).

#### 3. Results and discussion

#### 3.1. Cyclization of citronellal

The citronellal cyclization to isopulegols (Fig. 1, route 1) was studied on different Lewis acids, under which especially  $ZnBr_2$  is industrial applied, heteropoly acids as well as different solid acids such as zeolites and self-prepared sulfated zirconia ( $ZrO_2$ -SO<sub>4</sub>). Note that Lewis acids and heteropoly acids are soluble under given conditions. Conversion of citronellal ( $X_{CAL}$ ), selectivities to isopulegols ( $S_{ISPs}$ ), defunctionalization ( $S_{DFP}$ ) and dimerization products ( $S_{Dimers}$ ) as well as the ratio of isopulegol:neo-isopulegol:iso-isopulegol:neoiso-isopulegol are compared in Table 1.

In addition to the desired cyclization of citronellal to isopulegol, dimerization of citronellal via aldol condensation (Fig. 1, route 4b). dimerization of isopulegol to di-isopulegol ethers (Fig. 1, route 4c). and the defunctionalization of isopulegols to p-menthadienes (Fig. 1, route 4a) were observed. This is consistent with previous works [12,13]. No reaction of citronellal occurred on activated carbon and oxides such as SiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>. Sulfated zirconia showed the highest activity of the investigated catalysts. Already after 5 min, a conversion of 98% was reached. However, a large amount of dimerization products and a small amount of p-menthadienes were formed. This leads to a selectivity to isopulegols of only 59%. High conversions of >99% after 1 h were also reached with heteropoly acids (phosphomolybdic acid and phosphotungstic acid). Again, the fraction of dimerization products was high leading to isopulegols of <70% selectivity. Using Lewis acids such as ZnBr<sub>2</sub>, ZnCl<sub>2</sub>, FeCl<sub>3</sub>, and SnCl<sub>2</sub>, conversions of 33–98% were obtained after 1 h. ZnBr<sub>2</sub>, ZnCl<sub>2</sub>, and SnCl<sub>2</sub> exhibited selectivities to isopulegols of 93-96%, whereas with FeCl<sub>3</sub>, only 68% was reached. The highest selectivities to isopulegols (>98%) were obtained with Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and the zeolites H-BEA and H-ZSM5. Among them, H-BEA was also highly active (citronellal conversion >99%). Note that the Si:Al ratio of H-BEA had no effect on the conversion and product distribution. The amount of acid sites of H-BEA-25, H-ZSM5, and sulfated zirconia, determined by temperature-programmed desorption of NH<sub>3</sub>, increased in the following order:  $ZrO_2-SO_4$  (0.69 mmol g<sup>-1</sup>) < H-BEA-25 (1.11 mmol g<sup>-1</sup>) < H-ZSM5 (1.99 mmol g<sup>-1</sup>). No correlation of the citronellal conversion with the amount of acid sites was observed, which indicates pore-diffusion limitation of citronellal and isopulegols in the small zeolite pores [13]. Beside the amount of acid sites, acid strength of zeolites is another parameter, which also depends on the Si:Al ratio: an increase of the latter results in an increase of the acid strength of

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Table	1

#	Catalyst	X <sub>CAL</sub> (%)	$S_{\rm ISPs}$ (%)	S <sub>DFP</sub> (%)	S <sub>Dimers</sub> (%)	ISP:n-ISP:i-ISP:ni-ISP
1	H-BEA (Si:Al = 25, 35, 150)	99	98	<1	2	69:26:4:1
2	H-ZSM5 (Si:Al = 27)	34	97	<1	3	44:50:3:3
3	ZrO <sub>2</sub> -SO <sub>4</sub> <sup>b</sup>	98	59	1	40	48:47:3:2
4	Al <sub>2</sub> O <sub>3</sub> —SiO <sub>2</sub>	54	99	0	1	68:25:5:2
5	ZnBr <sub>2</sub>	77	96	<1	3	93:2:5:0
6	ZnCl <sub>2</sub>	41	95	<1	5	90:5:5:0
7	FeCl <sub>3</sub>	98	68	<1	32	66:29:4:1
8	SnCl <sub>2</sub>	33	93	<1	6	64:31:4:2
9	$H_{3}PMo_{12}O_{40}$	>99	67	<1	33	61:34:4:2
10	$H_3PW_{12}O_{40}$	>99	68	<1	32	56:38:4:2
11	$SiO_2$ , $La_2O_3$ , $Al_2O_3$ , $TiO_2$ and activated carbon	<1	99	<1	<1	-

Activity, selectivity and stereoselectivity of different types of catalysts in the cyclization of citronellal to isopulegol.<sup>a</sup>

<sup>a</sup> Reaction conditions: 0.5 mL citronellal, 50 mg catalyst, 10 mL *n*-hexane, 1 mL *n*-tetradecane, 353 K, 1 h.

<sup>b</sup> After 5 min.

the single active site. However, with increasing Si:Al ratio, the amount of acid sites decreases. Both opposite effects lead to a maximum of acidity. Indeed, decreasing amount of acid sites with increasing Si:Al ratio was also found for H-BEA zeolites [27]. Because we did not observe a dependency of the catalytic properties on the Si:Al ratio for the three H-BEA zeolites of the present study, we did not further characterize these non-modified zeolites by means of NH<sub>3</sub>-TPD, but the metal/H-BEA-25 catalysts (Table 2), and we did not use, for example, <sup>1</sup>H magic angle spinning (MAS) NMR and FTIR spectroscopy of probe molecules to estimate the strength of acid sites and to differentiate between Brønstedt and Lewis acid sites of the zeolites. For solid catalysts which are known to exhibit high acid strength, for example, ZrO<sub>2</sub>-SO<sub>4</sub>, cyclization vields low diastereoselectivity toward the desired isopulegol and is accompanied by the formation of considerable amounts of dimers (40%, Table 1), i.e. isopulegol ethers (Fig. 1, route 4b).

Note that all catalysts produced the desired isopulegol as the predominant isomer, followed by neo-isopulegol, iso-isopulegol, and neoiso-isopulegol (Table 1). Only isopulegol has all substituents of the cyclohexane ring in an equatorial position and, thus, this configuration is about 15 kJ mol<sup>-1</sup> more stable than neoisopulegol [13]. However, the experimental determined distribution of the four stereoisomers strongly depends on the nature of the catalyst; thereby, the amount of isopulegol in the total amount of all isopulegol isomers decreased in the order ZnBr<sub>2</sub> > ZnCl<sub>2</sub> >  $FeCl_3 > SnCl_2$ . As described above, these catalysts are soluble in *n*-hexane and, thus, the disadvantages of a homogenous catalyst prevail. Therefore, taking into account all data, H-BEA zeolites are the most promising solid acids for the cyclization of citronellal to isopulegol due to the high stereoselectivity of 69%, very high activity and the small amounts of by-products (Table 1). In the next step, they were used in combination with a metal for the synthesis of menthol by one-pot transformation of citronellal.

#### 3.2. One-pot transformation of citronellal to menthols

#### 3.2.1. Effect of the metal

The one-pot transformation of citronellal to menthols (Fig. 1, routes 1 and 2) was investigated on Pd-, Pt-, and Ru-supported H-BEA with a Si:Al ratio of 25 (H-BEA-25). In each case, a loading of 2 wt% was used. The particle size of the metals differed strongly. With 12.4 nm, the Pd particles on H-BEA-25 were larger than the Pt and Ru particles with a size of 2.7 and 1.4 nm, respectively (Table 2). Fig. 2 summarizes the citronellal conversion ( $X_{CAL}$ ), the selectivities to menthols ( $S_{MTs}$ ), isopulegols ( $S_{ISPs}$ ), hydrogenation products (dihydrocitronellal (DHC), citronellol (COL), and 3,7-dimethyloctanol (DMO)), defunctionalized products ( $S_{DFP}$ ), dimers ( $S_{Dimers}$ ), and the diastereoselectivity to menthol ( $x_{MT}$ ) after 40 min.

Already after 40 min, a citronellal conversion of more than 99% was achieved with all metal/H-BEA-25 catalysts, but the product distribution differed strongly. Using Pd/H-BEA-25, the selectivity to menthols remained 40%, whereas selectivity to cyclic dimerization products (Fig. 1, route 4c) of 9% and selectivity to hydrogenation products (DHC, DMO; Fig. 1, route 3) of 25% was obtained. Interestingly, Pd/H-BEA also catalyzed defunctionalization reactions leading to relatively high amounts of defunctionalization products ( $S_{DFP} = 25\%$ ). Neatu et al. [24] reached a menthol selectivity of 30% with a 3%Pd/H-BEA catalyst (353 K, 15 bar, cyclohexane as solvent). However, no defunctionalization products were described.

On Pt/H-BEA-25, high selectivities to menthols of 78% were achieved. Reaction products of citronellal hydrogenation (DHC, DMO), defunctionalization (DFP), dimerization, and non-converted isopulegol account for the difference in selectivity to 100%. In contrast to Pd/H-BEA-25, no cyclic products due to isopulegol dimerization but exclusively citronellal dimerization products were obtained. The menthol selectivity agrees with the results of Mertens et al. [22], who obtained menthols and isopulegols with a selectivity of 71.7% and 5.4%, respectively (2%Pt/H-BEA, 353 K, 20 bar, cyclohexane as solvent). With a 3%Pt/H-BEA catalyst, Neaţu et al. [24] obtained menthols with a selectivity of 56% (353 K, 15 bar, cyclohexane as solvent). These differences can be ascribed to the strong dependency of the obtained selectivities on the reaction conditions.

Using Ru/H-BEA, high selectivities to menthols and the parent isopulegols of 43% and 19%, respectively, were reached. With a 3%Ru/H-BEA catalyst, Neaţu et al. [24] obtained menthols with a selectivity of only 20% and isopulegols with a selectivity of 18% (353 K, 15 bar, cyclohexane as solvent). These differences can also be ascribed to the strong dependency of the obtained selectivities on the reaction conditions (see Section 3.2.2 Ru/H-BEA.) Hydrogenation of citronellal also occurred, but instead of the C=C bond, the C=O group of citronellal was hydrogenated, which is typical for Ru instead of Pd, to form citronellol. The latter was hydrogenated to 3,7-dimethyloctanol in a further consecutive reaction. In sum, a

#### Table 2

Metal particle size calculated from CO chemisorption measurements and amount of acid sites determined by temperature-programmed desorption of  $\rm NH_3$  of metal/H-BEA.

#	Catalyst	Metal particle size (nm)	Amount of acid sites (mmol $g^{-1}$ )
1	H-BEA-25	-	1.11
2	2%Pd/H-BEA-25	12.4	n.d.
3	2%Pt/H-BEA-25	2.7	1.02
4	2%Ru/H-BEA-25	1.4	0.81



**Fig. 2.** Influence of the metal on the product distribution of the transformation of citronellal to menthol on metal/H-BEA-25 catalysts. Reaction conditions: 4.5 g CAL, 0.5 g 2%metal/H-BEA-25, 150 mL *n*-hexane, 1 mL *n*-tetradecane, 25 bar, 373 K, t = 40 min.

selectivity to hydrogenation products of 34% was obtained after 40 min. Note that with Ru/H-BEA, defunctionalization and citronellal dimerization can be almost avoided (1% and 4%, respectively).

As largest fraction of the defunctionalized products p-menthenes were obtained on all metals. The p-menthenes were hydrogenated to p-menthanes during the reaction.

Note that neither Neaţu et al. [24] nor Mertens et al. [22] described the formation of dimerization and defunctionalization products.

Beside the hydrogenation of C=C, C=O double, and CN triple bonds, Pd is often used for hydrogenolysis, whereas using Pt and Ru, the C-O and N-O bonds normally retained [28]. Therefore, the amount of defunctionalized products was significantly higher on Pd than on Pt- and Ru-supported H-BEA.

A metal sensitivity of the hydrogenation of citronellal is confirmed by the different hydrogenation products formed on the different metals. Whereas on Pd and Pt, the C=C double bond of citronellal is hydrogenated to dihydrocitronellal, Ru hydrogenates, as mentioned before, the C=O group of citronellal to citronellol, which agrees with the literature [28-30]. However, using Ru significantly, more hydrogenation products of citronellal were formed than with Pt. An ion exchange of  $H^+$  of the zeolite with Ru during the preparation can be suggested by the decreased amount of acid sites of the catalyst measured by NH<sub>3</sub>-TPD compared to pure H-BEA (Table 2). Note that the Pt precursor  $(Pt(acac)_2)$  was dissolved in toluene, while Ru and Pd were impregnated via an aqueous precursor solution of Ru(NO<sub>3</sub>)<sub>3</sub>NO and Pd(NO<sub>3</sub>)<sub>2</sub>, respectively. Those solutions are also used for catalyst preparation via ion exchange [31,32]. Consequently, less acid sites are present for the cyclization of citronellal on Ru/H-BEA-25 and, thus, more hydrogenation products were formed. On Pt/H-BEA, the desired stereoisomer (±)-menthol was obtained as the predominant isomer. With a fraction of 69%, it agrees with the distribution of isopulegols in the cyclization of citronellal (Table 1, entry 1). Similar menthol content (73%) in the total amount of menthol isomers was observed with Ru/H-BEA-25. This level was outperformed by Pd/H-BEA-25 with 87%. These amounts correlated with the large content of defunctionalization and dimerization products shown in Fig. 2. A favored defunctionalization of neo-menthol is indicated by the decreasing fraction of neo-menthol and the increasing fraction of menthol, especially on Pd, in course of time (Fig. 3).

Summarized, Ru and Pt are suitable metals for the one-pot transformation of citronellal to menthol. Using these metal/ H-BEA-25 catalysts, high selectivities to menthols are achieved, whereas with Pd defunctionalization and dimerization of menthols predominate. In the next step, the influence of several conditions (with respect to catalyst and reaction) on the one-pot transformation of citronellal to menthols on Ru/H-BEA catalysts, not previously investigated in the literature, was studied in detail.

#### 3.2.2. Ru/H-BEA

3.2.2.1. Effect of Ru loading and Si:Al ratio of the zeolite. The effect of the loading was investigated on Ru-supported H-BEA-25, H-BEA-35, and H-BEA-150. Loadings of 1, 2, and 4 wt% were used. The particle size determined by CO chemisorption measurements increased with the Ru loading as expected (Table 3).

For example, the Ru particle size on H-BEA-25 increased in the following order: 1.0 nm (1 wt%) < 1.4 nm (2 wt%) < 2.7 nm (4 wt%). Furthermore, the size of the Ru particles also depended on the Si:Al ratio of the zeolite: for each Ru loading, the metal particle size increased with increasing Si:Al ratio (Table 3). NH<sub>3</sub> desorption and pyridine adsorption measurements showed the lower the Si:Al ratio the more (especially Brønstedt) acidic the zeolite [33]. Thus, more H<sup>+</sup> are available for an ion exchange, and consequently, the particles are smaller.

Table 4 summarizes the citronellal conversion ( $X_{CAL}$ ), the overall selectivities to menthols ( $S_{MTs}$ ), isopulegols ( $S_{ISPs}$ ), hydrogenation products ( $S_{Hyd.}$ ), defunctionalized products ( $S_{DFP}$ ), dimers ( $S_{Dimers}$ ), and the diastereoselectivity to menthol ( $x_{MTI}$ ) after 40 min as well as the maximum selectivity to menthols with the corresponding time in parentheses. In addition, the turnover frequency (TOF) of the hydrogenation of isopulegols to menthols is represented.

From an analysis of these reaction data under the given conditions, the following principal conclusions can be drawn: (i) menthol selectivity increases with increasing Si:Al ratio at each of the three Ru loadings (entry 1,2,3 vs. 4,5,6 vs. 7,8,9) reaching 66% with 4%Ru/H-BEA-150, (ii) after 40 min, menthol content in the fraction of all menthol isomers (diastereoselectivity) is independent on Ru loading and Si:Al ratio and amounts to 67–73%, (iii) isopulegol selectivity decreases with Ru loading/Ru particle size (entry 1,4,7 vs. 2,5,8 vs. 3,6,9) and also, in the case of 1 wt% Ru, with increasing Si:Al ratio (entry 1,2,3), (iv) at each of the three loadings the TOF increases with increasing Si:Al ratio because Ru particle size increases with the latter, and (v) inverse to isopulegol formation the selectivity to hydrogenation products (DHC, COL, DMO) increases with increasing Ru loading, as expected; thereby, this effect is more pronounced with H-BEA-25, i.e. at low Si:Al ratio



**Fig. 3.** Fraction of menthol ( $x_{MT}$ ) and neo-MT ( $x_{n-MT}$ ) in course of time on metal/H-BEA-25 catalysts. Reaction conditions: 4.5 g CAL, 0.5 g 2%metal/H-BEA-25, 150 mL *n*-hexane, 1 mL *n*-tetradecane, 25 bar, 373 K.

Table	3
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Ruthenium particle size dependent on Ru loading and Si:Al ratio of H-BEA.

	Ru particle size	(nm)		
	1 wt% Ru	2 wt% Ru	4 wt% Ru	
H-BEA-25	1.0	1.4	2.7	
H-BEA-35	1.4	2.0	3.7	
H-BEA-150	2.1	2.4	11.1	

(entry 1,4,7). However, at high Ru content (4 wt%), hydrogenation is diminished with increasing Si:Al ratio (entry 7,8,9).

Note that the maximum selectivity to menthols ( $S_{MTs,max}$ ) is time dependent for different Ru loadings: on 4%Ru/H-BEA-25, for example, the maximum selectivity of 37% was reached after 140 min, whereas using 1 wt% Ru, at the same Si:Al ratio, a maximum selectivity of 77% was reached but at considerably prolonged reaction time (240 min).

A similar effect of the loading was observed on Pt/H-BEA catalysts [22]. Ir/H-BEA catalysts show a different behavior [24]. In this case, a loading of 3 wt% represents a maximum in the menthol selectivity. These differences can be traced back to the reduction degree of the active metal. While assuming reduced Ru and Pt particles, Ir particles are partially oxidized and therefore, the hydrogenation of isopulegols occurs slowly.

Although only minor amounts of defunctionalization products (DFP) were observed with Ru/H-BEA catalysts (Table 4, maximum 6% at Si:Al = 150 and with the largest Ru particles), it is interesting to compare DFP with menthol formation. A trend to defunctionalization products due to conversion of menthols becomes apparent (Fig. 4).

On 2%Ru/H-BEA-35 and 2%Ru/H-BEA-150, the selectivity to menthols increased till a maximum, i.e. at higher Si:Al ratio larger reactions times lead to menthol defunctionalization. In contrast, the selectivity to menthols on 2%Ru/H-BEA-25 increased slowly, but then remains constant. This agrees with the high amounts of defunctionalized products obtained on the large Pd particles (d = 12.4 nm) of Pd/H-BEA (Fig. 3; Table 2) indicating a structure-sensitivity of the defunctionalization. The interaction between the OH group of menthol and Ru may be stronger on larger metal particles, and therefore, defunctionalization of menthols becomes more important. Although structure-sensitivity of defunctionalization must be proved in a separate study, the reaction of another OH group containing compound, namely glycerol, over Ru catalysts exhibiting different degrees of Ru dispersion, clearly shows that degradation is preferred over larger Ru particles [34].

Summarized, a high selectivity to menthols can be obtained with low Ru loadings, but the time needed to yield the desired product is increased because of the decreased reaction rate. Thus,



**Fig. 4.** Selectivity to menthols (MTs) and defunctionalization products (DFP) in course of time on 2%Ru/H-BEA catalysts with different Si:Al ratios. Reaction conditions: 4.5 g CAL, 0.5 g 2%Ru/H-BEA, 150 mL *n*-hexane, 1 mL *n*-tetradecane, 25 bar, 373 K.

for further investigations, a loading of 2 wt% was used. The higher the Si:Al ratio of the zeolite the faster the reaction and the higher the maximum selectivity to menthols. Thus, for further investigations, a Si:Al ratio of 150 was used.

3.2.2.2. Effect of temperature and pressure. The effect of the reaction temperature was investigated between 333 K and 393 K on the 2%Ru/H-BEA-150 catalyst selected before (Table 5, entries 1–4). Table 5 summarizes the citronellal conversion after 40 min ( $X_{CAL}$ ), the selectivities to menthols ( $S_{MTs}$ ), isopulegols ( $S_{ISPs}$ ) and by-products (DHC, COL, DMO, DFP and dimers), the diastereoselectivity to menthol ( $x_{MT}$ ) as well as the maximum selectivity to menthols ( $S_{MTs,max}$ ) with the corresponding time in parentheses. Furthermore, the turnover frequency (TOF) of the hydrogenation of isopulegols to menthols is represented.

The TOF increased with the temperature  $(1.0 \text{ min}^{-1} \text{ at } 333 \text{ K to} 9.3 \text{ min}^{-1} \text{ at } 393 \text{ K})$  strongly influencing the product distribution. At low temperatures, the hydrogenation of citronellal (Fig. 1, route 3) was favored leading to high amounts ( $S_{Hyd.} = 56\%$ ) of citronellol and 3,7-dimethyloctanol at 333 K. In contrast, defunctionalization (Fig. 1, route 4a) did not play an important role at lower temperatures up to 373 K. At higher temperatures, cyclization of citronellal was preferred to its hydrogenation, producing less amounts of

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Effect of Ru loading and Si:Al ratio on citronellal conversion, product selectivities and turnover frequencies of menthol formation in the one-pot synthesis of menthol.<sup>a</sup>

#	Catalyst	X <sub>CAL</sub> (%)	S <sub>MTs</sub> (%)	x <sub>MT</sub> (%)	$S_{\rm ISPs}$ (%)	$S_{\rm Hyd.}{}^{\rm b}$ (%)	S <sub>DFP</sub> (%)	S <sub>Dimers</sub> (%)	$S_{MTs,max}$ (%) ( $t$ (min))	$TOF^{c}$ (min <sup>-1</sup> )
1	1%Ru/H-BEA-25	91	19	72	63	16	2	1	77 (240)	1.6
2	1%Ru/H-BEA-35	99	32	67	46	15	2	5	75 (180)	2.8
3	1%Ru/H-BEA-150	95	40	71	38	18	1	3	74 (150)	4.8
4	2%Ru/H-BEA-25	99	43	73	19	34	1	4	60 (150)	1.3
5	2%Ru/H-BEA-35	99	55	69	20	20	2	3	70 (60)	5.4
6	2%Ru/H-BEA-150	99	52	72	25	21	1	2	71 (60)	6.6
7	4%Ru/H-BEA-25	100	36	71	3	56	1	4	37 (140)	0.9
8	4%Ru/H-BEA-35	100	55	68	1	37	4	4	55 (40)	5.9
9	4%Ru/H-BEA-150	100	66	73	0	26	6	2	67 (20)	43.3

<sup>a</sup> Reaction conditions: 4.5 g CAL, 0.5 g Ru/H-BEA, 373 K, 25 bar, 150 mL *n*-hexane, 1 mL *n*-tetradecane, *t* = 40 min.

<sup>b</sup>  $S_{\text{Hyd.}} = S_{\text{DHC}} + S_{\text{COL}} + S_{\text{DMO}}$ .

<sup>c</sup> The TOF refers to the hydrogenation of isopulegols to menthols at the point of the maximum selectivity to menthols. The amount of active sites is obtained from CO uptake of the CO chemisorption measurements.

citronellol and 3,7-dimethyloctanol at 393 K where also defunctionalization became important. Note that at 333 K and 393 K, isopulegols were totally converted to menthols after 180 min and 40 min, respectively. The highest selectivity to menthols of 71% was obtained at 373 K after 60 min. At this temperature, the cyclization of citronellal was fast enough to avoid large amounts of citronellal hydrogenation products (DHC, COL, DMO). These results agree with the effects observed on Pt/H-BEA and Ir/H-BEA catalysts. It confirms the assumption of the higher apparent activation energy of the cyclization of citronellal than the hydrogenation [22,24].

Using the 2%Ru/H-BEA-150 catalyst, the hydrogen pressure was varied between 15 and 45 bar (Table 5, entry 3,5,6). The TOF increased with hydrogen pressure (1.4 min<sup>-1</sup> at 15 bar to 8.6 min<sup>-1</sup> at 45 bar). At 45 bar, isopulegol conversion is almost complete already after 40 min in contrast to 270 min at 15 bar. As expected. the higher the hydrogen pressure the higher the amount of hydrogenation products. Thus, the maximum selectivity to menthols raised with decreasing pressure: from 62% at 45 bar to 75% at 15 bar. This effect can be explained by the solubility of hydrogen in *n*-hexane. Due to the increasing solubility at higher pressures [35], the amount of hydrogen in the solution increases, and therefore, more hydrogenation products are formed. The desired menthol stereoisomer was produced predominantly with diastereoselectivity ( $x_{MT}$ ) of 70%, excluded at 393 K and 25 bar (Table 5, entry 4), where even  $x_{MT}$  achieved 80%. Note that this level is correlated with the relatively high amount of defunctionalized products  $(S_{\text{DFP}} = 13\%)$ . As described above, neo-menthol was defunctionalized first, leading to an adjustment of the stereoisomers in favor of the desired menthol. It can be concluded that high selectivities to menthols can be obtained at low hydrogen pressure and higher temperatures to avoid hydrogenation products of citronellal. Defunctionalization decreases with lower temperatures, and consequently, a temperature of 373 K represents an optimum.

3.2.2.3. Effect of solvent. In addition to *n*-hexane, the solvents acetonitrile, toluene, tetrahydrofuran, and dioxane were used for the transformation of citronellal to menthol on the 2%Ru/H-BEA-150 catalyst. Fig. 5 shows the citronellal conversion ( $X_{CAL}$ ), the selectivities to menthols ( $S_{MTs}$ ), isopulegols ( $S_{ISPs}$ ), hydrogenation products (dihydrocitronellal (DHC), citronellol (COL), and 3,7-dimethyloctanol (DMO)), defunctionalized products ( $S_{DFP}$ ), dimers ( $S_{Dimers}$ ), and the diastereoselectivity to menthol ( $x_{MT}$ ) after 40 min.

In acetonitrile, there is an unexpectedly dramatic loss of catalyst activity indicated by CAL conversion as shown in Fig. 5. The presence of isopulegol (in minor amount), iso-citronellal, and dimers and the complete absence of menthols implies loss of active sites for the cyclization step, i.e. of acid (Brønstedt) sites which can occur via protonation of the CN group of acetonitrile. In toluene and *n*-hexane, a maximum selectivity to menthols of 71% was obtained. Hydrogenation products (Fig. 1, route 3) predominated in *n*-hexane, whereas defunctionalization prevailed in toluene (Fig. 1, route 4a). In tetrahydrofuran and dioxane, the highest selectivities to menthols of 90% were reached. Interestingly, no dimerization was observed in dioxane.

Similar results were obtained with Pt/H-BEA catalysts. Using dioxane, the highest menthol yields were obtained, while using the non-polar solvent cyclohexane, high amounts of hydrogenation products were obtained [22]. In contrast, cyclohexane led to the best selectivities with an Ir/H-BEA catalyst [24].

The amount of hydrogenation products correlated with the solubility of hydrogen in the different solvents. Under reaction conditions (373 K, 25 bar), the solubility of hydrogen decreases in the following order: *n*-hexane > toluene  $\approx$  tetrahydrofuran > dioxane [35], and in the same order, the amount of hydrogenation products decreased. The stereochemistry was also affected by the solvent. In *n*-hexane and toluene, the amount of menthol in the total amount of menthols was 72%. in tetrahydrofuran only 65% and in dioxane even 78%. Actually, the prediction/discussion of the direct influence of a solvent on stereoselectivity in the case of a heterogeneously catalyzed reaction, even in a three-phase system such as menthol synthesis (and in the presence of a bifunctional catalyst), is rather complicated because this requires knowledge of solvated transition state structures. The change of the solvent changes the solvation which modifies the adsorption strength of all reactants/products within the complicated reaction network. In this sense, the influence on stereoselectivity can be also indirectly induced, for example, by suppressing non-desired reactions. Indeed, Fig. 5 shows that in the presence of *n*-hexane and toluene, the selectivity toward DMO and DFP is increased, respectively, leading to a decreased MT selectivity, and vice versa. It can be concluded that dioxane and tetrahydrofuran are suitable solvents for the one-pot transformation of citronellal to menthol on Ru/H-BEA catalysts; however, in dioxane, the desired menthol diastereoisomer dominated.

Note that no clear dependencies between catalyst activity, product selectivity, or time to reach maximum menthol selectivity and solvent properties in terms of permittivity and dipole moment were observable.

3.2.2.4. Combination of appropriate conditions. Based on the results described above, the most promising conditions were combined to obtain a maximum menthol selectivity. Low Ru loading and low hydrogen pressure proved to diminish the non-desired hydrogenation of citronellal (Fig. 1, route 3). A Si:Al ratio of H-BEA of 25 as well as a temperature of 373 K minimized defunctionalization of menthols (Fig. 1, route 4a). Dioxane as solvent proved to avoid hydrogenation as well as dimerization of citronellal. Fig. 6 shows the most promising results (entry 1–3) as well as the results of the combined conditions (entry 4–5).

The maximum selectivity raised from 71% on 2%Ru/H-BEA-150 (1) to 77% on 1%Ru/H-BEA-25 in *n*-hexane at 25 bar and 373 K (3). Using dioxane as solvent, the maximum selectivity is further

Table 5

Effect of reaction temperature and pressure on citronellal conversion, product selectivities and turnover frequencies of menthol formation in the one-pot synthesis of menthol.<sup>a</sup>

#	T (K)	$p_{\rm H2}~({\rm bar})$	X <sub>CAL</sub> (%)	$S_{\rm MTs}$ (%)	x <sub>MT</sub> (%)	$S_{\rm ISPs}$ (%)	S <sub>Hyd.</sub> <sup>b</sup> (%)	S <sub>DFP</sub> (%)	S <sub>Dimers</sub> (%)	$S_{\mathrm{MTs,max}}$ (%) ( $t$ (min))	$TOF^{c}$ (min <sup>-1</sup> )
1	333	25	64	17	74	23	56	0	3	33 (180)	1.0
2	353	25	90	21	70	41	33	1	5	57 (150)	2.1
3	373	25	99	52	72	25	21	1	2	71 (60)	6.6
4	393	25	99	67	80	2	16	13	2	67 (40)	9.3
5	373	15	96	17	70	71	10	1	0	75 (270)	1.4
6	373	45	99	62	70	1	32	3	2	62 (40)	8.6

<sup>a</sup> Reaction conditions: 4.5 g CAL, 0.5 g 2%Ru/H-BEA-150, 150 mL *n*-hexane, 1 mL *n*-tetradecane, 40 min.

<sup>b</sup>  $S_{\text{Hyd.}} = S_{\text{DHC}} + S_{\text{COL}} + S_{\text{DMO}}$ .

<sup>c</sup> The TOF refers to the hydrogenation of isopulegols to menthols at the point of the maximum selectivity to menthols. The amount of active sites is obtained from CO uptake of the CO chemisorption measurements.



**Fig. 5.** Influence of the solvent on selectivity, conversion and diastereoselectivity ( $x_{MT}$ ). Reaction conditions: 4.5 g CAL, 0.5 g 2%Ru/H-BEA-25, 150 mL solvent, 1 mL *n*-tetradecane, 25 bar, 373 K, *t* = 60 min (hexane), 40 min (acetonitrile), 180 min (toluene), 120 min THF, 60 min (dioxane).

increased to 90% on a 2%Ru/H-BEA-150 at 25 bar and 373 K (2). Obviously, the solvent affects the selectivity much more than the loading and Si:Al ratio. Accordingly, a very high selectivity of 93% was reached using 1%Ru/H-BEA-25 at a pressure of 15 bar, a temperature of 373 K and dioxane as solvent (5). Fig. 7 shows the product distribution during the reaction on (a) 2%Ru/H-BEA-150 in *n*-hexane at 25 bar and 373 K (1) and (b) 1%Ru/H-BEA-25 in dioxane at 15 bar and 373 K (5).

The observed concentration-time dependency was expected from the reaction scheme shown in Fig. 1. In a first step, citronellal is cyclized to isopulegol (Fig. 1, route 1), which is hydrogenated to menthols (Fig. 1, route 2). This leads to the typical concentrationtime dependency of a consecutive reaction. In case of a fast cyclization of citronellal, only small amounts of the undesired hydrogenation products are formed (Fig. 1, route 3).

Because of the higher pressure and the higher Ru loading, citronellal was converted faster under the conditions of Fig. 7a. But high amounts of undesired hydrogenation products of citronellal (DHC, COL, and DMO) were produced. After 60 min, dihydrocitronellal



**Fig. 6.** Combination of appropriate conditions (Ru loading, Si:Al ratio, pressure, solvent, reaction time) to obtain maximum selectivity to menthols. Reaction conditions: 4.5 g CAL, 0.5 g Ru/H-BEA, 150 mL solvent, 1 mL *n*-tetradecane, 373 K: (1) 2%Ru/H-BEA-150–25 bar – *n*-hexane – 60 min, (2) 2%Ru/H-BEA-150–25 bar – dioxane – 60 min, (3) 1%Ru/H-BEA-25–25 bar – *n*-hexane – 240 min, (4) 1%Ru/H-BEA-25–25 bar – *n*-hexane – 360 min, (5) 1%Ru/H-BEA-25–15 bar – *n*-hexane – 360 min.



**Fig. 7.** Concentration of citronellal, isopulegols, menthols and by-products during the one-pot transformation of citronellal to menthols. Reaction conditions: 4.5 g CAL, 0.5 g catalyst, 150 mL *n*-solvent, 1 mL *n*-tetradecane, 373 K, (a) 2%Ru/H-BEA-150, *n*-hexane, 25 bar; (b) 1%Ru/H-BEA-25, dioxane, 15 bar.

and citronellol were totally converted to dimethyloctanol and the maximum selectivity to menthols of 71% was reached. Afterward, menthols were defunctionalized as described above. Because the dimerization of citronellal is faster than the dimerization of isopulegols and menthols, about 80% of the total dimerization products were obtained during the first 30 min. However, it must be noted that under the conditions of Fig. 7b, no dimerization products were produced. The reaction is now highly selective: citronellal was converted to menthols with a selectivity of 93%, and because reactions leading to by-products were eliminated the concentration vs. time plot is now simplified and typical for a consecutive reaction  $CAL \rightarrow ISPs \rightarrow MTs$ . Only a small amount of dihydrocitronellal and citronellol was formed and further converted to dimethyloctanol during the reaction. Defunctionalization did not predominate. In conclusion, low Ru loadings, low hydrogen pressure, and a low Si:Al ratio in addition to dioxane as solvent are required to obtain high menthol selectivities.

## 4. Conclusion

The one-pot transformation of citronellal (CAL) to menthols (MTs) was successfully achieved with bifunctional Ru/H-BEA catalysts. In a first step, several solid acids and Lewis acids were investigated in the cyclization of citronellal to isopulegols (ISPs). Zeolite

H-BEA proved to be the most promising heterogeneous catalyst because of the less formation of by-products, high selectivity  $(S_{ISPs} = 98\%)$ , and the high content (69%) of the desired isopulegol in the fraction of all isopulegol isomers. Next, the one-pot cyclization of citronellal to menthols was investigated using bifunctional H-BEA catalysts exhibiting hydrogenation properties in terms of Pd, Pt, or Ru for the ISP  $\rightarrow$  MT step. After evaluating their performance with respect to reactions which must be avoided (MT defunctionalization, CAL and ISP dimerization, CAL hydrogenation), Ru/H-BEA catalysts, which were not investigated in the literature yet, were studied in detail to get deeper insight into the effect of catalyst composition (Si:Al ratio, Ru content) and reaction conditions (temperature, hydrogen pressure, solvent). The higher the Ru loading the higher the amount of hydrogenation products leading to lower menthol selectivities. Furthermore, the higher the Si:Al ratio the higher the maximum selectivity to menthols. However, with increasing Si:Al ratio, the amount of defunctionalized products is increased. A temperature of 373 K avoids CAL hydrogenation which predominates at lower temperatures, as well as defunctionalization, which is significant at higher temperatures. In addition, the solvent has an enormous influence on the product distribution. Using the solvents dioxane and tetrahydrofuran, the highest selectivities to menthols are obtained; however in dioxane, the desired menthol diastereoisomer is preferred. Choosing appropriate conditions (1%Ru/H-BEA-25, 373 K, 15 bar, dioxane as solvent), a very high menthol selectivity of 93% can be obtained on Ru/H-BEA. Using this new catalyst/reaction system, the amount of the desired diastereomer (±)-menthol in the fraction of all menthol isomers reached 79%.

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