Menthol via Heterogeneous Catalysis:
Highly Selective Menthol Synthesis by One-Pot Transformation of Citronellal
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Introduction
With an annual production of about 20,000 tons menthol is one of the world’s most common aroma compounds with a broad range of applications (e.g., in toothpastes, tobacco, chewing gum) [1]. Because of its three asymmetric carbon atoms in the cyclohexane ring, menthol has four stereoisomeric pairs (Figure 1). But only (–)-menthol has the typical strong odour and the characteristic cooling effect [2]. Consequently, the other stereoisomers as well as (+)-menthol are less valuable and undesired. While natural menthol exists as the pure (-)-menthol [2], for synthetic menthol it is either necessary to treat the racemic menthol in a separation crystallization process (Harrmann-Reimer process) or to use a chiral homogeneous catalyst (Takasago and BASF process) [1, 3]. The use of heterogeneous catalysts is both environmental friendly and can be industrially a more attractive alternative for the production of fine chemicals due to the easy separation and the reuse of these catalysts.

We report here on our ongoing research to produce menthol with heterogeneous catalysts via a one-pot transformation of citronellal to menthol. 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. Using this new catalyst/reaction system a very high menthol selectivity of 93 % can be obtained and the amount of the desired diastereomer (±)-menthol in the fraction of all menthol isomers reached 79 % [4]. Figure 2 compares the concentration of CAL, ISPs, MTs and by-products (defunctionalization (DFP) and hydrogenation products) during the reaction choosing initial conditions (Figure 2-left: 2%Ru/H-BEA-150, 373 K, 25 bar, n-hexane as solvent) and appropriate conditions (Figure 2-right: 1%Ru/H-BEA-25, 373 K, 15 bar, dioxane as solvent).

Materials and Methods
Supported metal catalysts were obtained by incipient-wetness impregnation of different types of zeolite H-BEA (Clariant) as supports using Ru(NO)(NO₃)₃ (Alfa Aeser) as metal precursor and water as solvent. The catalytic experiments were carried out in a batch reaction vessel (Parr Co.). Usually, racemic citronellal (c = 0.19 mol L⁻¹ in n-hexane) was transformed at 373 K and a pressure of 25 bar. Samples were taken periodically and analyzed by gas chromatography (HP 6890, DB-Wax) using n-tetradecane as internal standard.

Results and Discussion
Bifunctional Ru/H-BEA catalysts were used 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. Using this new catalyst/reaction system a very high menthol selectivity of 93 % can be obtained and the amount of the desired diastereomer (±)-menthol in the fraction of all menthol isomers reached 79 % [4]. Figure 2 compares the concentration of CAL, ISPs, MTs and by-products (defunctionalization (DFP) and hydrogenation products) during the reaction choosing initial conditions (Figure 2-left: 2%Ru/H-BEA-150, 373 K, 25 bar, n-hexane as solvent) and appropriate conditions (Figure 2-right: 1%Ru/H-BEA-25, 373 K, 15 bar, dioxane as solvent).

Figure 2: Concentration of CAL, ISPs, MTs and by-products during the transformation of CAL to MTs.

Significance
Choosing appropriate conditions it is possible to obtain menthol via a heterogeneous catalyzed one-pot transformation of citronellal with a yield of 93%.

References