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A tandem cyclization and hydrogenation of (±)-citronellal to menthol over bifunctional Ni/Zr-beta and mixed Zr-beta and Ni/MCM-41

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Abstract

The addition of nickel to Zr-beta gave a useful bifunctional catalyst that combines a high rate of cyclization of (±)-citronellal to isopulegols over zirconium sites and subsequent hydrogenation to menthols. The diastereoselectivity to the desired (±)-menthol was 90%. A loading of 4 wt% is optimal; lower loadings led to a low rate of hydrogenation, whereas a higher nickel loading appears to block the zirconium Lewis acid sites essential for the cyclization of citronellal. A mixture of Zr-beta and Ni/MCM-41 also formed an effective bifunctional catalyst system where the selectivity toward menthols remained high even with nickel loadings up to 15 wt%. The yield of (±)-menthol over the dual-catalyst system was 86–89% with <5% of byproducts, citronellol and 3,7-dimethyloctanol. Besides nickel, bifunctional Rh/Zr-beta catalysts also formed menthols with selectivity >93%, although the diastereoselectivity to (±)-menthol was lower (85%). In comparison, a 2% Pd/Zr-beta catalyst exhibited lower activity and selectivity to menthols, forming substantial amounts of 3,7-dimethyloctanal.

Keywords: Zr-beta; Bifunctional catalyst; Nickel; Rhodium; (±)-Citronellal; (±)-Menthol; Diastereoselectivity

1. Introduction

(−)-Menthol is an important material in the fragrance industry due to its characteristic peppermint odor [1,2]. It is widely used in pharmaceuticals, cosmetics, toothpastes, chewing gum, cigarettes, and other products. (−)-Menthol is isolated from natural sources, such as the oil of *Mentha arvensis* or *Mentha piperita*. (−)-Menthol can also be synthesized from other terpenoids such as (+)-citronellal, citral, (+)-pulegone, (+)-limonene, (+)-β-pinene, and (+)-δ-2-carene. The cyclization of (±)-citronellal **1** gives four stereoisomers of isopulegol, each of which occurs as a pair of enantiomers: (±)-isopulegol **2**, (±)-neo-isopulegol **3**, (±)-iso-isopulegol **4**, and (±)-neoiso-isopulegol **5** (Scheme 1). Hydrogenation of these isopulegols leads to four pairs of enantiomers: (±)-menthol **6**, (±)-neomenthol **7**, (±)-isomenthol **8**, and (±)-neoisomenthol **9**. Of these, (−)-menthol **6** has the most perceptible cooling effect, and hence its selective synthesis is desired.

The cyclization of citronellal to isopulegols proceeds readily over a number of homogeneous as well as heterogeneous catalysts [3–10]. Zinc bromide, which gives 94% selectivity to (−)-isopulegol **2**, is used industrially. However, stoichiometric amounts of zinc bromide are required for adequate activity and the presence of bromide may lead to corrosion problems. A recent patent to Takasago International Corporation disclosed the use of another homogeneous catalyst, tris(2,6-diarylphenoxy)aluminum, which gives almost exclusively (−)-isopulegol **2**, 99.3% [11]. Homogeneous catalysts require extensive workup, and thus the catalysts often cannot be recovered and reused. In contrast, the heterogeneous catalysts that have been described in the literature (e.g., zeolite beta, MCM-41, HY, mordenite) offer ease of recovery of isopulegols and catalyst reuse, but the diastereoselectivity to (±)-isopulegol **2** is generally low (52–76%) [8–12]. One approach to improving diastereoselectivity was to immobilize $ZnBr_2$ on SiO_2. Depending on the pretreatment temperature, selectivities to (−)-isopulegol **2** of 72–86% were reported [7]. Promising results have also been obtained with Sn-beta [13] and Zr-beta zeolites [14], with diastereoselectivity to (±)-isopulegol **2** of 85 and 93%, respectively. The higher diastereoselectivity found

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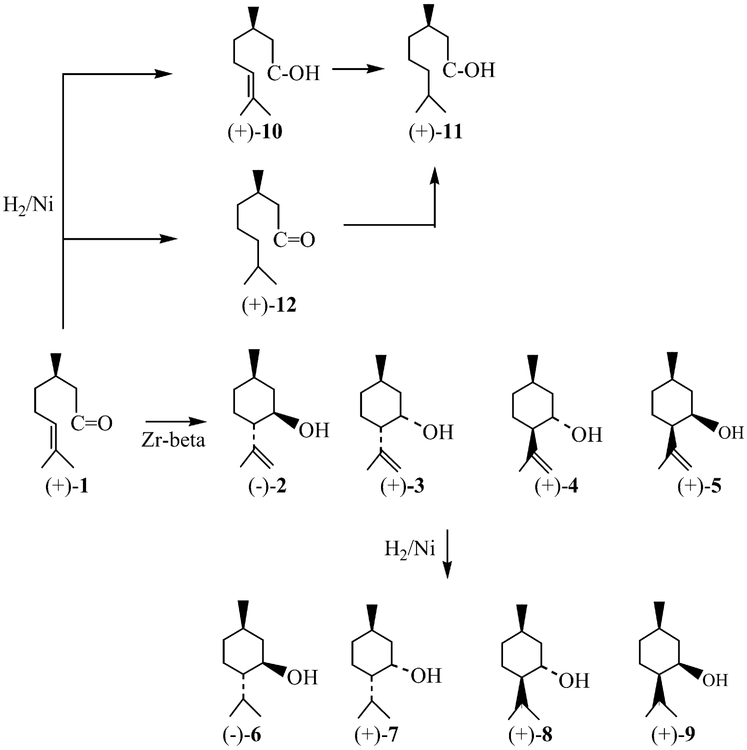

Scheme 1. Products formed in the hydrogenation of citronellal.

with these zeolites as compared with Al-beta (∼71%) was attributed to the size of the metal ion in the microporous channels. Replacing Al^{3+} by the bigger Zr^{4+} ion in the framework of zeolite beta restricts the pore space, thus affecting the selectivity toward the different isomers in the cyclization process.

The combined cyclization to isopulegols and hydrogenation to menthols has been described by Milone et al. [15] for ruthenium on different supports. The silica support had to be acidified to be active for the cyclization of citronellal. At 100% conversion of citronellal, the yield of menthols was 80%, but a rather substantial amount of the fully hydrogenated product, 3,7-dimethyloctanol **11**, was formed. Activated carbon was a poor support, even after treatment with HCl. Due to the lack of acid sites, the rate of cyclization was low, and only a 30% combined yield of all menthol isomers was obtained. The addition of $ZnBr_2$ to Ru/SiO_2 improved the selectivity to (−)-isopulegol **2**, reaching 86% selectivity for Zn loading $\geqslant 4$ mmol/g SiO_2 [16]. Ravasio et al. [17] reported that the hydrogenation of (+)-citronellal into menthols over silica-supported copper catalysts required very mild conditions of 0.1 MPa H_2 pressure and 90 °C. Another active catalyst was beta zeolite impregnated with iridium, giving a high yield of menthols (93–95%) [18]. Those authors found beta zeolite to be a better support for iridium than mordenite with nonreduced iridium ions contributing to the isomerization activity. However, the diastereoselectivity to (±)-menthol **6** was only 75% with 20% (±)-neomenthol **7** and 5% (±)-isomenthol **8**. An increase in the diastereoselectivity from 78.9 to 88.0% was reported for a 2 wt% Pt/H-beta sample after calcination and reduction at 750 °C [19]. It was suggested that this heat treatment converted some of the Brønsted acid sites to Lewis acid sites, thus affecting the isomeric ratio.

In this study, we combined the high diastereoselectivity for the conversion of (±)-citronellal **1** to (±)-isopulegol **2** of Zr-beta with hydrogenation activity to achieve a tandem synthesis of menthols from citronellal. We have reported previously [20] that Zr-beta-supported nickel catalysts show high selectivity for the hydrogenation of (±)-citronellal to menthols, forming (±)-menthol **6** in high excess. In this paper, we present detailed characterization data for Zr-beta- and MCM-41-supported nickel catalysts. The activity and selectivity of bifunctional Ni/Zr-beta catalysts, as well as dual-catalytic systems of Zr-beta & Ni/MCM-41, are optimized and compared. Other metals, such as palladium, copper, and rhodium, are also investigated.

2. Experimental

2.1. Catalyst preparation and characterization

Purely siliceous MCM-41 was prepared as follows. Tetraethylammonium hydroxide (TEAOH) solution (40% in water) and cetyltrimethylammonium bromide (CTMABr) were added to deionized water, and the solution was heated slightly until it became clear. Fumed silica was then added, and the solution was kept at 70 °C with stirring for another 2 h. After aging at 25 °C for 24 h, the mixture was placed in a Teflon-lined stainless steel autoclave and heated for 48 h at 150 °C. The molar composition of the final gel mixture was 1.0 SiO_2:0.19 TEAOH:0.27 CTMABr:40 H_2O. The product was