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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.
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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
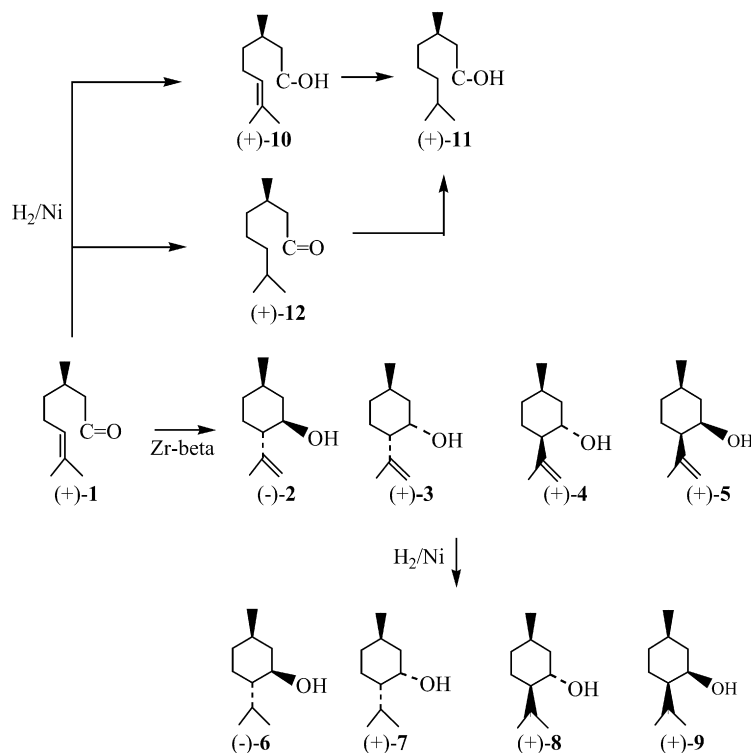
Scheme 1. Products formed in the hydrogenation of citronellal.

with these zeolites as compared with Al-beta ($\sim$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$4 mmol/g SiO_2 [16]. Ravasio et al. [17] reported that the hydrogenation of ($+$)-citronellal into menthols over silica-supported copper catalysts required very mild conditions of 0.1 MPa H_2 pressure and 90 °C. Another active catalyst was beta zeolite impregnated with iridium, giving a high yield of menthols (93–95%) [18]. Those authors found beta zeolite to be a better support for iridium than mordenite with nonreduced iridium ions contributing to the isomerization activity. However, the diastereoselectivity to ($\pm$)-menthol 6 was only 75% with 20% ($\pm$)-neomenthol 7 and 5% ($\pm$)-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 ($\pm$)-citronellal 1 to ($\pm$)-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 ($\pm$)-citronellal to menthols, forming ($\pm$)-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

filtered, washed with deionized water, dried in air at 90 °C, and finally calcined at 550 °C for 8 h.

The synthesis of aluminum-free Zr-zeolite beta (Si/Zr 100) has been described previously [21]. The catalyst was prepared in a fluoride-assisted hydrothermal synthesis with the addition of seeds from dealuminated zeolite beta, similar to the procedure described by Corma et al. [22] for the preparation of Al-free Sn-beta. Typically, tetraethylorthosilicate (TEOS) was hydrolyzed in a solution of TEAOH under stirring. A solution of $ZrOCl_2 \cdot 8H_2O$ in water was added, and the mixture was stirred until all ethanol formed by hydrolysis of the TEOS was evaporated. Hydrogen fluoride and an aqueous suspension of dealuminated nanocrystalline zeolite beta seeds were added. The composition of the final gel was 1 SiO_2:0.01 ZrO_2:0.56 TEAOH:0.56 HF:7.5 H_2O. Crystallization was carried out in a static Teflon-lined stainless steel autoclave at 140 °C for 20 days. The solid product obtained was filtered, washed with deionized water, dried at 100 °C, and calcined at 580 °C for 4 h.

Nickel supported on Zr-beta (Ni/Zr-beta) and MCM-41 (Ni/MCM-41) were obtained by incipient-wetness impregnation of the support with an aqueous solution of $Ni(NO_3)_2$ at 30 °C. The metal loadings on Zr-beta were varied from 3 to 15 wt% and from 1 to 30 wt% on MCM-41. After impregnation, the samples were dried overnight at 90 °C and calcined in air at 450 °C for 6 h. A 8 wt% Cu sample was prepared by impregnating MCM-41 with copper acetate solution, followed by drying and calcination at 400 °C for 4 h. A 2% Pd/Zr-beta sample was prepared similarly by wet impregnation of the support with palladium chloride dissolved in ammonia, dried, and calcined at 300 °C for 4 h. Rhodium chloride was impregnated onto the Zr-beta support to give Rh loadings of 0.25, 0.5, and 2 wt%. These samples were dried and subsequently calcined at 550 °C for 4 h. Before catalytic measurements, the nickel catalysts were reduced in H_2 (50 ml/min) for 2 h at 450 °C. Rhodium, copper, and palladium catalysts were reduced in a H_2/He mixture (50:50) for 4 h at 300, 270, and 150 °C, respectively.

The surface area and pore volumes were measured by nitrogen adsorption (Micromeritics Tristar). The samples were degassed in N_2 at 300 °C before measurement. The surface area was calculated from the BET equation, and the microporous surface areas and micropore volumes were determined from the t-plot analysis. The total pore volume was determined from N_2 adsorption at $P/P_0 > 0.99$. The crystal phase was determined with a Siemens D5005 powder X-ray diffractometer equipped with a Cu anode and variable primary and secondary beam slits. Transmission electron microscopy (TEM) measurements were performed with a JEOL JEM3010 HRTEM at 300 kV. The finely ground sample was suspended in ethanol, and a drop was mounted onto a copper grid and dried before the TEM measurements.

2.2. Catalytic testing

The catalytic tests were performed at 80 °C in a Teflon-lined stainless steel autoclave using 1.7 ml (9.5 mmol) of (±)-citronellal, 50 ml of *tert*-butanol, and 0.15 g of freshly reduced

Table 1
Textural properties of catalysts[a]

Sample	Surface area (m^2/g)	Micropore surface area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	Crystallite size[b] (nm)
Zr-beta	476	402	0.25	0.20	–
3% Ni/Zr-beta	453	386	0.25	0.19	–
4% Ni/Zr-beta	439	377	0.24	0.19	22
5% Ni/Zr-beta	436	369	0.24	0.18	30
15% Ni/Zr-beta	421	346	0.24	0.17	33
MCM-41	948	35.4	0.91	0.02	–
3% Ni/MCM-41	947	33.6	0.90	0.02	–
5% Ni/MCM-41	838	33.2	0.81	0.02	–
10% Ni/MCM-41	787	34.5	0.75	0.02	11
15% Ni/MCM-41	659	39.9	0.69	0.02	8.0
30% Ni/MCM-41	548	24.3	0.55	0.02	18
8% Cu/MCM-41	812	33.5	0.77	0.02	–
0.25% Rh/Zr-beta	463	384	0.26	0.19	–
0.5% Rh/Zr-beta	473	403	0.26	0.20	–
2.0% Rh/Zr-beta	443	358	0.26	0.17	–
2.0% Pd/Zr-beta	340	301	0.22	0.15	–

[a] After calcination.
[b] Calculated from Debye–Scherrer equation ($d = 0.9\lambda/\beta\cos\theta$, where d = crystallite size, $\lambda = 0.15418$ nm, β = corrected full-width half maximum, θ = diffraction angle).

catalyst at a hydrogen pressure of 2 MPa. A lower hydrogen pressure of 0.5 MPa was used for the Rh/Zr-beta catalysts. For the dual-catalyst system, both 0.15 g and 0.30 g of a 1:1 mixture of Zr-beta and Ni/MCM-41 were tested. Typically, the reaction was conducted in a He atmosphere with stirring for the first hour to allow the cyclization of citronellal to isopulegols. After 1 h, the He atmosphere was replaced with H_2. Samples were removed at regular intervals and analyzed by gas chromatography (HP5 column).

3. Results and discussion

3.1. Textural properties

The physical properties of the catalysts are summarized in Table 1. The surface area of Zr-beta (Si/Zr 100) was reduced only slightly (up to 11%) after impregnation with nickel. The loss in surface area is due to partial blockage of the micropores, with a decrease in the microporous volume observed (Fig. 1). However, the total pore volume, which includes the interparticle pores, remained relatively unchanged. The powder XRD patterns of Ni/Zr-beta catalysts were similar to that of the pure support, with characteristic peaks of zeolite beta at $2\theta \sim 7.55°$, 22.4°, and 43.55°. Hence, impregnation did not destroy the crystalline structure of Zr-beta. Additionally, the nickel phase could be observed for reduced Zr-beta with 4 to 15 wt% nickel (Fig. 2). From the Debye–Scherrer equation, the size of the nickel crystallites was calculated as 22–33 nm, depending on the metal loading.

MCM-41 had a surface area of 948 m^2/g, which is about twice that of Zr-beta (Table 1). The surface area decreased after impregnation with nickel. This decrease was more drastic than that for Zr-beta, with a loss of 30% for the 15 wt% Ni sample. Nonetheless, the XRD patterns showed that MCM-41 retained
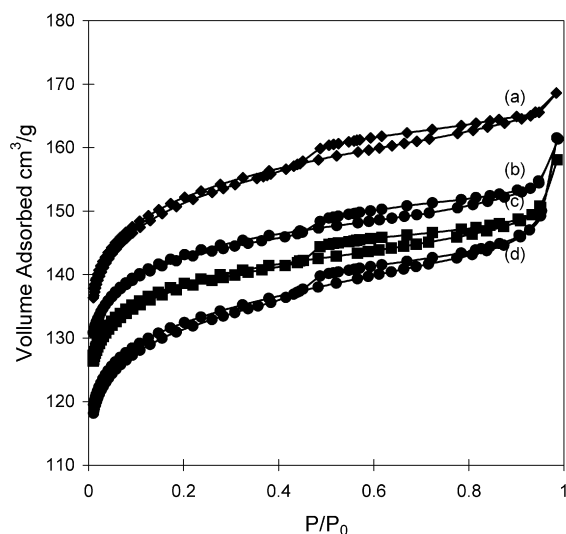
Fig. 1. Nitrogen porosimetry of (a) Zr-beta, (b) 3% Ni/Zr-beta, (c) 4% Ni/Zr-beta, and (d) 15% Ni/Zr-beta.

Fig. 2. X-ray diffraction patterns of (a) 3% Ni/Zr-beta, (b) 4% Ni/Zr-beta, (c) 5% Ni/Zr-beta, and (d) 15% Ni/Zr-beta. Reflections of metallic nickel indicated by ∗.
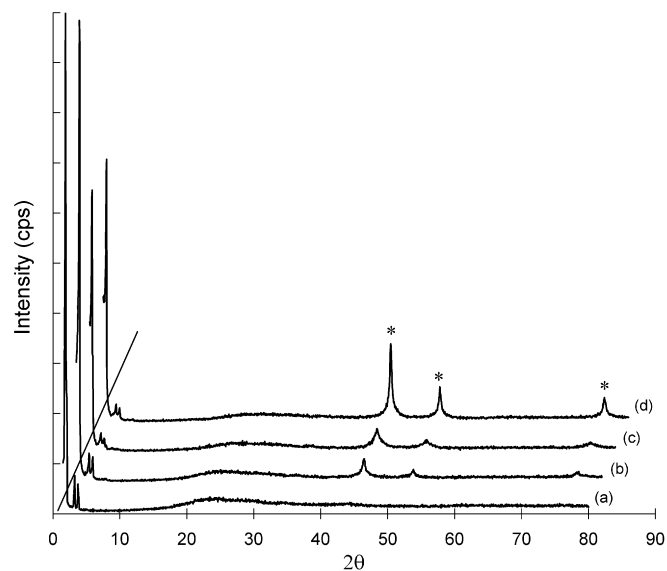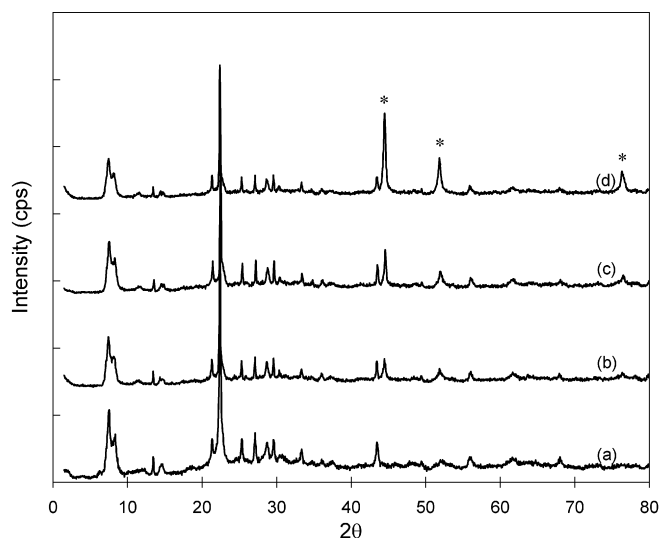

Fig. 3. X-ray diffraction patterns of (a) 3% Ni/MCM-41, (b) 10% Ni/MCM-41, (c) 15% Ni/MCM-41, and (d) 30% Ni/MCM-41. Reflections of metallic nickel indicated by ∗.

black dots, are well distributed over the Zr-beta and MCM-41 supports. Nickel clusters in the samples with low metal loading had a narrow size distribution around 4–5 nm, whereas the cluster size is less uniform in samples with higher loadings. In addition to the small clusters, these samples also contain clusters with diameters up to 30–40 nm. These values agree reasonably well with the volume average particle sizes calculated from the Debye–Scherrer equation (Table 1). For Zr-beta with microporous channels of ∼0.6–0.7 nm, these visible nickel clusters must be located on the external surface. Due to rapid electron beam-induced sample degradation in the TEM, any smaller nickel particles that might exist inside the pores cannot be imaged.

3.2. Catalytic activity of Zr-beta & Ni/MCM-41

A dual-catalyst system of Zr-beta and Ni/MCM-41 was tested for the one-pot transformation of (±)-citronellal **1** to menthols. The use of MCM-41 allows a high metal dispersion on the mesoporous support. A 1:1 ratio of each component was used with a total weight of either 150 or 300 mg. The nickel loading was varied from 1 to 30 wt%. Fig. 5a shows the course of reaction over a Zr-beta & 15%Ni/MCM-41 system. The reaction was carried out under helium for the first hour before hydrogen was introduced. The initial rate of the (±)-citronellal cyclization was about twice that for hydrogenation, hence the major products formed after 2 h were isopulegols with (±)-isopulegol **2**, (±)-neo-isopulegol **3**, and (±)-iso-isopulegol **4** in a ratio of 94:5:1. No (±)-neoiso-isopulegol **5** was detected. Beyond this reaction time, the rate of hydrogenation to menthols increased rapidly, so that after 7 h, most of the isopulegols were converted to menthols. The hydrogenation of the isopulegols did not lead to any significant change in the diastereoselectivity so that the desired (±)-menthol **6** was formed with a selectivity of 93% relative to all of the menthol isomers (Ta-

its structure after impregnation. The presence of nickel could be observed only for loadings of 10 wt% or higher (Fig. 3). The diffraction peaks of nickel were generally broad, leading to an average crystallite size on the order of 8–18 nm for loadings of 10–30 wt%. This is two to three times smaller than on Zr-beta, indicating a higher metal dispersion on MCM-41. The difference in nickel crystallite sizes may be due to the hydrophobicity of the surfaces of Zr-beta. The synthesis of Zr-beta involves the use of HF instead of OH$^-$ as a mineralizer. This results in a hydrophobic material with very few Si–OH moieties [23]. These OH groups may act as nucleation sites for the deposition of the nickel salts. The predominantly hydrophilic MCM-41 offers a large number of surface OH groups, leading to more nucleation sites and therefore smaller crystallites.

Representative TEM micrographs of Ni-impregnated catalysts are shown in Fig. 4. The nickel clusters, represented by the
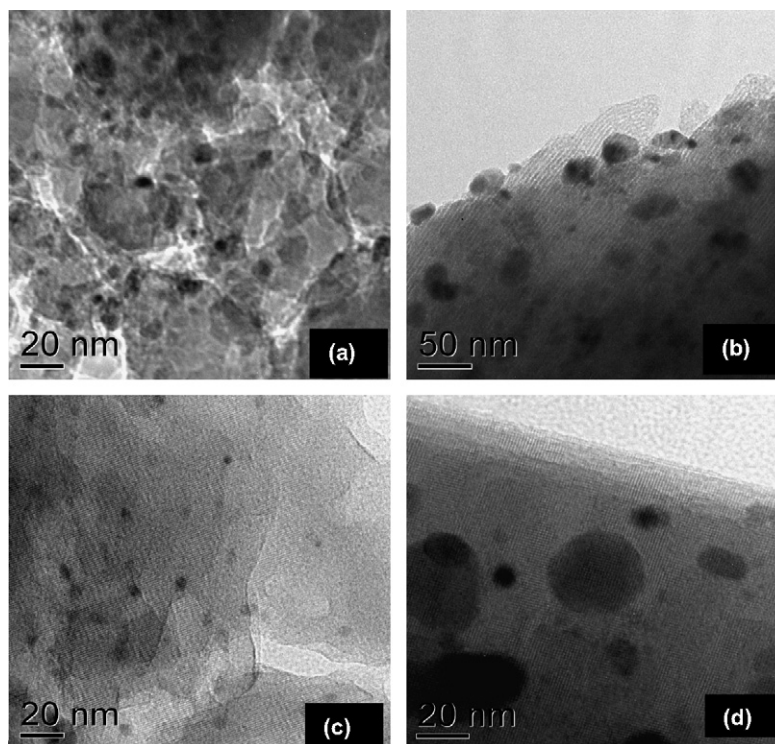
Fig. 4. TEM images of (a) 3% Ni/MCM-41, (b) 15% Ni/MCM-41, (c) 4% Ni/Zr-beta, and (d) 15% Ni/Zr-beta.
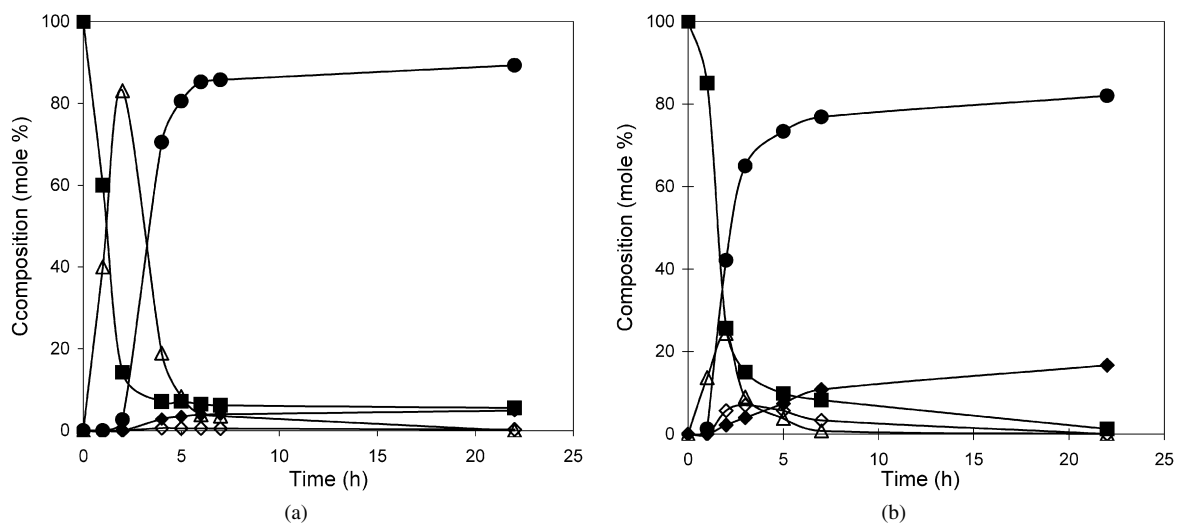

Fig. 5. Hydrogenation of (±)-citronellal over Zr-beta & 15% Ni/MCM-41 with H_2 introduced after (a) 1 h and (b) from start of experiment. (■) Citronellal, (△) isopulegol, (●) menthol, (◇) citronellol, and (◆) 3,7-dimethyloctanol. Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 0.30 g (0.15 g each) catalyst, 80 °C, (a) 2 MPa He for 1 h, followed by H_2; (b) 2 MPa H_2 from $t = 0$.

ble 2). Besides the isomeric menthols, other products of citronellal hydrogenation were detected. Citronellol **10** and 3,7-dimethyloctanol **11** were formed after an induction period, but their concentrations were <0.6 and 5%, respectively. The concentration of citronellol **10** reached a maximum at 4 h, and further hydrogenation of the C=C bond led to 3,7-dimethyloctanol **11**. No 3,7-dimethyloctanal **12** was observed, suggesting that over the Ni/MCM-41 catalyst, the carbonyl group in citronellal is preferentially hydrogenated rather than the C=C

bond, or that the transformation of 3,7-dimethyloctanal **12** to the 3,7-dimethyloctanol **11** is very fast.

When hydrogen was introduced from the start, the cyclization of (±)-citronellal still occurred in preference to hydrogenation to linear molecules (Fig. 5b). In fact, during the first hour, no hydrogenation products were observed. The maximum concentration of isopulegols was only 24%, compared with 87% when hydrogen was introduced after the first hour. Only after 2 h was a significant increase in menthols observed, together

Table 2
Product distribution in the hydrogenation of citronellal over dual catalysts Zr-beta & Ni/MCM-41

Entry	Catalyst	t (h)	Conversion (%)	Selectivity (%)				Yield (%)
				6–9 (6)	10	11	2–5	6–9 (6)
1	Zr-beta & 3% Ni[a]	8	94	92 (93)	0	3	5	86 (80)
		22	97	95 (93)	0	5	0	92 (86)
2	Zr-beta & 3% Ni	8	94	95 (93)	0	4	1	89 (83)
		22	97	95 (93)	0	5	0	92 (86)
3	Zr-beta & 5% Ni	8	94	95 (94)	0	4	1	89 (84)
		22	100	95 (94)	0	5	0	95 (89)
4	Zr-beta & 10% Ni	8	93	94 (93)	1	5	0	87 (81)
5	Zr-beta & 15% Ni[a]	7	93	91 (93)	1	4	4	85 (79)
		22	95	95 (93)	0	5	0	90 (84)
6	Zr-beta & 15% Ni	8	93	95 (94)	0	4	1	88 (83)
7	Zr-beta & 15% Ni[b]	7	92	84 (94)	3	12	1	77 (73)
8	Zr-beta & 30% Ni	7	96	92 (93)	0	5	3	88 (82)

Note. Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 0.3 g (0.15 g each of Zr-beta and Ni/MCM-41), 80 °C, 2 MPa H_2 after 1 h.

[a] 75 mg each of Zr-beta (Si/Zr 100) and Ni/MCM-41.

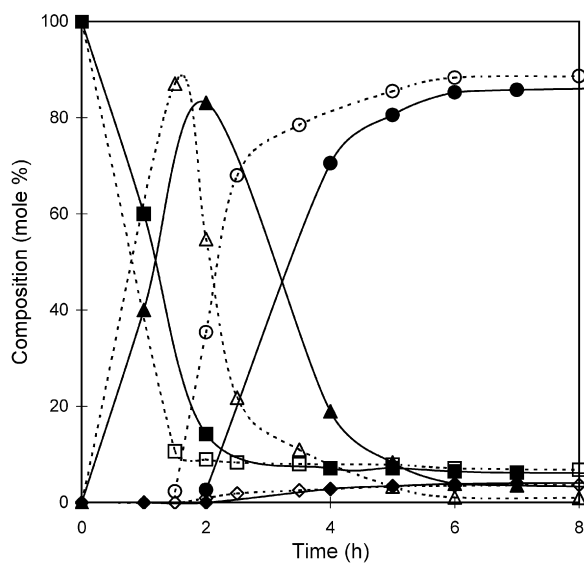[b] H_2 introduced from start of reaction.

Fig. 6. Comparison of different catalyst loading over Zr-beta & 15% Ni/MCM-41. Open symbols: 0.15 g each of Zr-beta and 15% Ni/MCM-41; closed symbols: 75 mg each of Zr-beta and 15% Ni/MCM-41. (■, □) Citronellal, (▲, △) isopulegols, (●, ○) menthols. Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 80 °C, 2 MPa H_2 after 1 h.
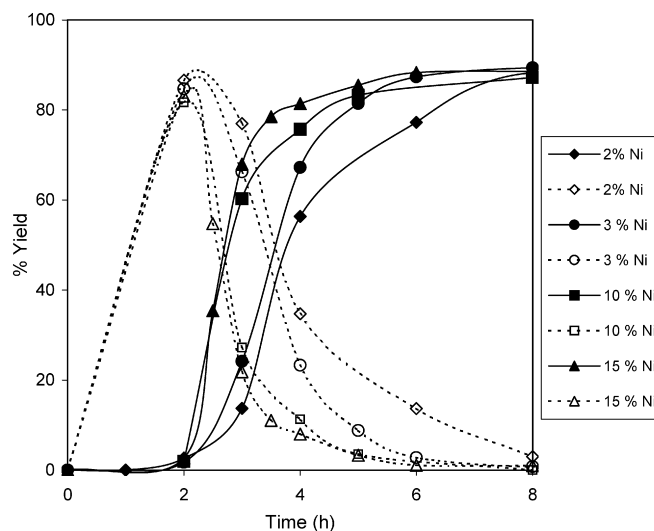

Fig. 7. Yields of isopulegols and menthols over Zr-beta & Ni/MCM-41 catalysts with different Ni loadings. Open symbols: isopulegols; closed symbols: menthols. Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 0.30 g (0.15 g each) catalyst, 80 °C, 2 MPa H_2 after 1 h.

with about 8% citronellol **10** and 3,7-dimethyloctanol **11**. After 22 h, the final products comprised 82% menthols and 17% 3,7-dimethyloctanol **11**. About 1% (±)-citronellal remained unconverted despite the long reaction time. The diastereoselectivity to (±)-menthol **6** was high (94%) and was not affected by the presence of hydrogen. Thus, delayed introduction of hydrogen is beneficial to maximize the yield of menthols and minimize the formation of byproducts. The high selectivity to menthols is aided by the fast kinetics for cyclization and the presence of an induction period for hydrogenation.

The effect of catalyst loading was also investigated. As expected, halving the amount of catalysts led to a lower rate of formation of isopulegols and menthols (Fig. 6). Complete hydrogenation of the isopulegols could be achieved only after

22 h, compared with 8 h for the reaction system with a greater catalyst weight.

Using the optimized reaction conditions, the effect of nickel loading on MCM-41 was investigated for the dual-catalytic system. While the rate of cyclization to isopulegols depended only on the amount of Zr-beta, increasing the Ni loading on MCM-41 led to a higher rate of hydrogenation of isopulegols to menthols (Fig. 7). For nickel loadings <2%, the isopulegols were not completely hydrogenated to menthols even after 22 h. However, a high loading of 30% Ni led to a lower rate of hydrogenation than that for 15% Ni/MCM-41. This may be due to the larger nickel crystallites formed on the former sample, 18 nm versus 8–11 nm for lower nickel loadings. Thus, the maximum rate was observed for 15% Ni/MCM-41. Despite the different hydrogenation activities, the selectivity to menthols was >92% for all Ni loadings, of which 93–94% was the
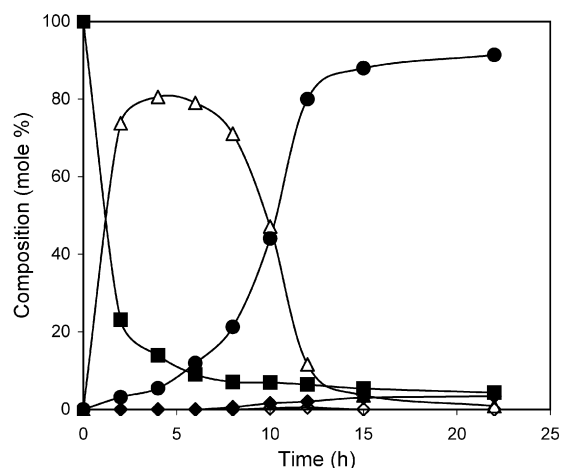
Fig. 8. Hydrogenation of (±)-citronellal over 4% Ni/Zr-beta. (■) Citronellal, (△) isopulegols, (●) menthols, (◇) citronellol, and (◆) 3,7-dimethyloctanol. Reaction conditions: 9.5 mmol citronellal, 50 ml *tert*-butanol, 0.15 g catalyst, 80 °C, 2 MPa H$_2$ after 1 h.

desired (±)-menthol isomer **6** (Table 2). The byproducts, 3,7-dimethyloctanol **11** and citronellol **10**, constituted <5% of the products.

3.3. Catalytic activity over bifunctional Ni/Zr-beta

Bifunctional catalysts capable of isomerization and hydrogenation were formed by impregnating Zr-beta with nickel. (±)-Citronellal **1** was rapidly converted over the bifunctional 4% Ni/Zr-beta catalyst, with conversion reaching 77% after only 2 h (Fig. 8). The main products, (±)-isopulegol **2**, (±)-neo-isopulegol **3**, and (±)-iso-isopulegol **4**, were detected in the ratio of 90:8:2. Only a small amount of menthols (3%) was observed at this time. Despite the nickel loading on the catalyst, the rate of cyclization to isopulegols was still higher than the rate of hydrogenation of citronellal to citronellol **10** and 3,7-dimethyloctanol **11**. These products appeared after 2 h of reaction time, and their concentrations increased to 0.5 and 3.6%, respectively, at longer reaction times. The high diastereoselectivity observed for (±)-isopulegol **2** was retained during hydrogenation, so that the desired (±)-menthol **6** was the predominant isomer. After 22 h, the yield of menthols was 92% at a citronellal conversion of 96%.

Increasing the nickel loading affected the cyclization of citronellal negatively but had a positive effect on hydrogenation. For the Zr-beta support, the initial rate at which isopulegols formed was 0.44 mmol/(g$_{cat}$ min), but over 3% Ni/Zr-beta and 15% Ni/Zr-beta, it was reduced to 0.35 and 0.20 mmol/(g$_{cat}$ min), respectively (Table 3). The drop in cyclization activity of the bifunctional catalyst can be attributed to nickel deposits that cover some of the zirconium required as active sites for cyclization. However, a higher nickel loading increased the rate of hydrogenation of isopulegols to menthols and also shortened the induction period (Fig. 9). At a low nickel loading of 3 wt%, isopulegols were still detected even after 22 h. For nickel loadings exceeding 5 wt%, the selectivity to menthols decreased as more open-chain hydro-
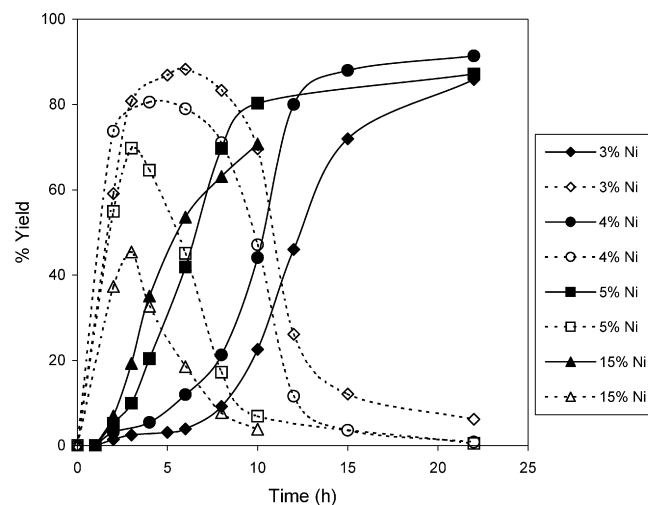

Fig. 9. Yields of isopulegols and menthols over bifunctional Ni/Zr-beta catalysts with different Ni loadings. Open symbols: isopulegols; closed symbols: menthols. Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 0.15 g catalyst, 80 °C, 2 MPa H$_2$ after 1 h.

Table 3
Initial rate of isopulegol formation over bifunctional Ni/Zr-beta samples

Catalyst	Initial rate (mmol/(g$_{cat}$ min))
Zr-beta	0.44
3% Ni/Zr-beta	0.35
4% Ni/Zr-beta	0.38
5% Ni/Zr-beta	0.29
15% Ni/Zr-beta	0.20

Note. Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 0.15 g catalyst, 80 °C, 2 MPa H$_2$.

Table 4
Product distribution in the hydrogenation of (±)-citronellal over bifunctional Ni/Zr-beta samples

Entry	Catalyst	*t* (h)	Conversion (%)	Selectivity (%)				Yield (%)
				6–9 (6)	**10**	**11**	**2–5**	**6–9 (6)**
1	3% Ni/Zr-beta	8	93	10 (90)	0	0	90	9.3 (8.4)
		22	95	90 (90)	0	3	7	86 (77)
2	4% Ni/Zr-beta	8	93	23 (91)	0	0	77	21 (19)
		22	96	96 (90)	0	3	1	92 (83)
3	5% Ni/Zr-beta	8	93	54 (90)	0	2	41	50 (45)
		22	96	90 (90)	6	1	3	86 (78)
4	15% Ni/Zr-beta	10	96	74 (86)	8	14	4	71 (61)

Note. Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 0.15 g catalyst, 80 °C, 2 MPa H$_2$ after 1 h.

genated byproducts formed. For 15% Ni/Zr-beta, citronellol **10** and 3,7-dimethyloctanol **11** constituted 22% of the final products (entry 4, Table 4). Thus, the highest selectivity to menthols (96%) was found for 4% Ni/Zr-beta. The diastereoselectivity to (±)-menthol **6** was 90% for catalysts with up to 5 wt% Ni, but only 86% for 15% Ni/Zr-beta. This suggests that the cyclization of citronellal could have occurred on external surfaces of the zeolite or on nickel crystallites where the directing effect due to the micropores was absent.

The hypothesis that cyclization of citronellal can occur over nickel crystallites was tested with 15% Ni/MCM-41 in helium.

Table 5
Cyclization of (±)-citronellal over MCM-41 and Ni/MCM-41

Catalyst	Gas	t (h)	Conversion (%)	Selectivity (%)				
				6–9 (6)	10	11	12	2–5 (2)
MCM-41	H$_2$	22	5.2	0	0	0	0	100 (83)
15% Ni/MCM-41	He	22	5.6	0	0	0	0	100 (83)
15% Ni/MCM-41	H$_2$	5	85	2 (81)	49	41	7	1 (82)
		22	94	2 (81)	0.7	96	1	0.3 (81)

Note. Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 0.15 g catalyst, 80 °C, 2 MPa H$_2$ or 0.4 MPa He.

Table 6
Effect of H$_2$ pressure over bifunctional Ni/Zr-beta and dual-catalyst Zr-beta & Ni/MCM-41

Catalyst	P (MPa)	t (h)	Conversion (%)	Selectivity (%)				Yield (%)
				6–9 (6)	10	11	2–5	6–9 (6)
5% Ni/Zr-beta	2	8	93	54 (90)	0	2	41	50 (45)
		22	96	90 (90)	6	1	3	86 (78)
	3	8	93	75 (91)	3	4	17	70 (63)
		22	96	91 (90)	2	7	0	87 (79)
Zr-beta & 15% Ni	2	7	93	91 (93)	0	4	4	85 (79)
	3	6	93	95 (94)	0	4	1	88 (83)

Note. Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 0.15 g catalyst (0.30 g for dual-catalyst system), 80 °C.

After 22 h, the (±)-citronellal conversion was 5.6%, similar to the 5.2% conversion observed over the siliceous MCM-41 support without Ni (Table 5). The diastereoselectivity to (±)-isopulegol **2** over both mesoporous samples was 81%. The comparable low yield of isopulegols found for both 15% Ni/MCM-41 and the MCM-41 support shows that Ni crystallites are unlikely to be involved in cyclization of citronellal. Moreover, when the reaction was conducted in the presence of H$_2$ with 15% Ni/MCM-41 as the catalyst, the bulk of the (±)-citronellal was converted to 3,7-dimethyloctanol **11**. The yield of menthols after 22 h was only 2%.

3.4. Effect of H$_2$ pressure

The effect of hydrogen pressure on the reaction was investigated for bifunctional Ni/Zr-beta and the dual-catalyst system (Table 6). When the H$_2$ pressure was below 2 MPa, the conversion of isopulegols to menthols over 5% Ni/Zr-beta was incomplete even after 22 h. Raising the H$_2$ pressure from 2 to 3 MPa increased the rate of hydrogenation but at the expense of a greater selectivity to citronellol **10** and 3,7-dimethyloctanol **11**. At 2 MPa, the main open-chain hydrogenation product was citronellol **10**, whereas at 3 MPa, more 3,7-dimethyloctanol **11** was present. In contrast, a higher H$_2$ pressure did not affect the selectivity to open-chain hydrogenation for the Zr-beta & 15% Ni/MCM-41 dual-catalyst system. Only 3,7-dimethyloctanol **11** was detected, and its selectivity remained low (4%). Thus, at 2–3 MPa H$_2$, the rate of cyclization was higher than the rate of hydrogenation for both catalytic systems, so that menthols formed >90% of the final products.
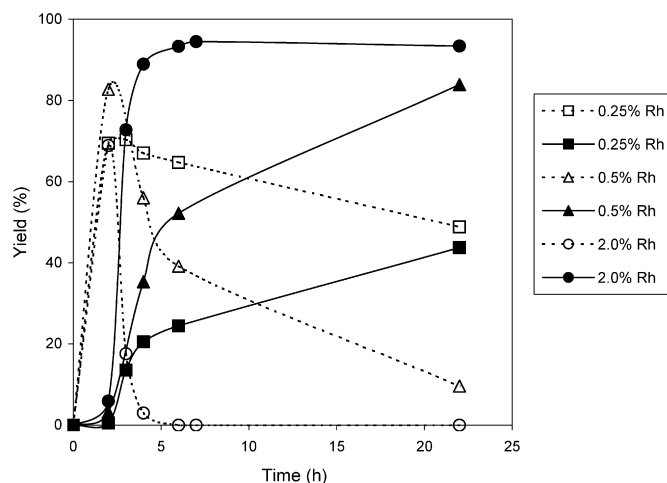

Fig. 10. Yields of isopulegols and menthols over bifunctional Rh/Zr-beta catalysts with different Rh loadings. Open symbols: isopulegols; closed symbols: menthols. Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 0.15 g catalyst, 80 °C, 0.5 MPa H$_2$ after 1 h.

3.5. Activity of other metals

The activity of other metals—copper, palladium, and rhodium—were tested and compared with that of the nickel samples. Over the mixed Zr-beta & 8% Cu/MCM-41 catalyst, only the cyclization of (±)-citronellal to isopulegols occurred. Less than 1% of the formed isopulegols were converted to menthols after 22 h, showing that the supported copper catalyst was rather inactive under these conditions (entry 1, Table 7). The transformation of (±)-citronellal to menthols was also slow over a 2% Pd/Zr-beta catalyst. The final products obtained at 97% conversion were 41% isopulegols, 24% menthols, and 32% 3,7-dimethyloctanal **12**. The formation of 3,7-dimethyloctanal **12** can be explained by the high activity of Pd catalysts for hydrogenation of the C=C bond rather than the C=O bond [24]. In comparison, bifunctional Zr-beta impregnated with rhodium forms an active catalyst that could hydrogenate the isopulegols under a relatively low pressure of 0.5 MPa. A loading of 2 wt% Rh allowed the conversion to reach >97% after only 6 h. Lower loadings of 0.25 and 0.5 wt% resulted in incomplete hydrogenation of isopulegols even after 22 h (Fig. 10). The selectivity to menthols was high (97%), with only one other product formed: 3,7-dimethyloctanol **11**. However, despite the high hydrogenation activity and high selectivity to menthols, the diastereoselectivity to (±)-menthol **6** was only 85%, lower than that found for supported Ni catalysts (Table 7). The decrease in diastereoselectivity and the observation that the rate of cyclization increased slightly with Rh loading suggest that Rh sites may contribute to the cyclization reaction. Similar observations have been reported for iridium supported on beta zeolite [18].

3.6. Catalyst reuse

Bifunctional 3% Ni/Zr-beta catalyst and Zr-beta & 3% Ni/MCM-41 were recycled by recalcining at 540 °C for 4 h and reduction in H$_2$ (Fig. 11). Although the conversion was un-

Table 7
Hydrogenation of (±)-citronellal over supported Cu, Pd, and Rh catalysts

Entry	Catalyst	t (h)	Conversion (%)	Selectivity (%) 6–9 (6)	10	11	12	2–5	Yield (%) 6–9 (6)
1	Zr-beta & 8% Cu/MCM-41[a]	22	98	1 (100)	0	5	0	94	1 (1)
2	2% Pd/Zr-beta[a]	29	91	24 (89)	1	2	32	41	21 (19)
3	0.25% Rh/Zr-beta	6	90	27 (94)	0	1	0	72	24 (23)
		22	94	47 (92)	0	1	0	52	44 (42)
4	0.5% Rh/Zr-beta	6	92	57 (89)	0	1	0	43	52 (47)
		22	95	89 (89)	0	1	0	10	84 (75)
5	2% Rh/Zr-beta	6	95	98 (85)	0	2	0	0	93 (79)
		22	100	93 (85)	0	7	0	0	93 (79)

Note. Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 0.15 g catalyst (0.30 g for dual-catalyst system), 80 °C, 0.5 MPa H_2 after 1 h.
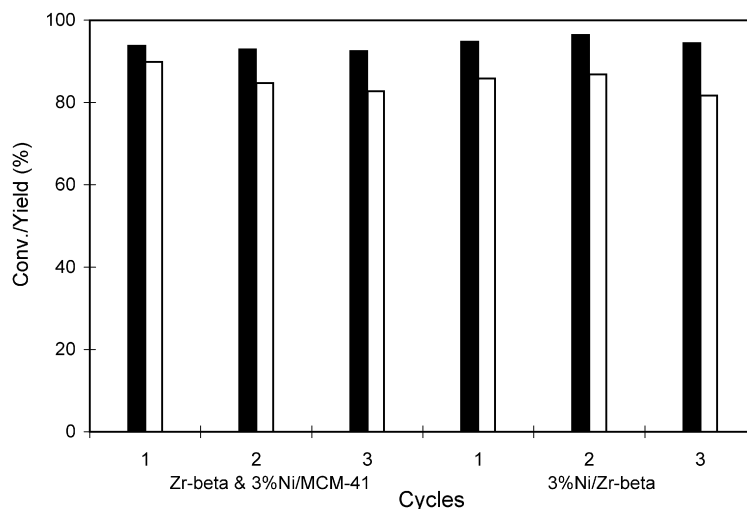[a] 2 MPa H_2 after 1 h.

Fig. 11. Reuse of Zr-beta & 3% Ni/MCM-41 and 3% Ni/Zr-beta catalysts measured after 5 and 22 h, respectively. Conversion (■) and yield of menthols (□). Reaction conditions: 9.5 mmol (±)-citronellal, 50 ml *tert*-butanol, 0.15 g catalyst (0.30 g Zr-beta & Ni/MCM-41), 80 °C, 2 MPa H_2 after 1 h.

changed, the yield to menthols was decreased slightly (by ∼4%) after three cycles. For the fresh Zr-beta & 3% Ni/MCM-41 and 3% Ni/Zr-beta, all of the isopulegols were already hydrogenated to menthols after 5 and 22 h, respectively. However, over the regenerated catalysts, isopulegols were still present at these reaction times, resulting in a lower yield of menthols. The recalcination and reduction treatment at high temperatures could have resulted in sintering of the nickel crystallites, thus decreasing the hydrogenation activity. Leaching of nickel can be ruled out, because no further conversion was observed after hot filtration of the catalyst from the reaction medium after 1 h. The general good tolerance to regeneration conditions of both catalytic systems makes them useful catalysts.

3.7. Comparison of the dual-catalyst system with the bifunctional Ni/Zr-beta system

The results show that at the same nickel loadings, the reaction rate and diastereoselectivity to (±)-menthol **6** was higher for the Zr-beta & Ni/MCM-41 system than for the bifunctional Ni/Zr-beta catalysts. The induction time (after the introduction of H_2) was reduced from 1–5 h with the bifunctional catalysts to 0.5–2 h in the dual-catalyst systems. In the bifunctional Ni/Zr-

beta, both rate and diastereoselectivity were affected by the partial coverage of some of the active sites on Zr-beta on Ni impregnation. In contrast, in the dual-catalyst system, the Zr-beta and Ni/MCM-41 catalysts were optimized for their respective functions of cyclization and hydrogenation. No intimate mixing of the two components was necessary for the selective hydrogenation of (±)-citronellal to menthols. The higher surface area of MCM-41 affords higher nickel dispersion with more active nickel sites per g catalyst, so that the rate of hydrogenation can be manipulated.

4. Conclusion

Impregnation of nickel on Zr-beta resulted in a bifunctional catalyst exhibiting high activity for the cyclization of (±)-citronellal to isopulegols and the subsequent hydrogenation of the formed isopulegols to menthols. The high diastereoselectivity to the (±)-isopulegol isomer **2** was maintained during the hydrogenation, so that (±)-menthol **6** was formed with ∼90% selectivity. A nickel loading of 3–5 wt% was effective for Zr-beta, but a higher loading of 15 wt% reduced the rate of cyclization but increased the rate of hydrogenation to form more byproducts, citronellol and 3,7-dimethyloctanol. In com-

parison, the one-pot dual-catalyst system composed of Zr-beta and Ni/MCM-41 gave a slightly higher diastereoselectivity to (±)-menthol **6**, 93–94%. The nickel loading could be increased up to 15% on MCM-41 without increasing the selectivity to byproducts.

Over both the bifunctional catalysts and the dual-catalyst system, the rate of cyclization of citronellal to isopulegols was faster than the rate of hydrogenation of citronellal, so that menthols were formed with high yields of 86–95%. Copper and palladium catalysts were not very active for the hydrogenation of isopulegols. A substantial amount of 3,7-dimethyloctanal was formed as a byproduct over the Pd/Zr-beta catalyst.

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