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Cyclization of citronellal over zeolites and mesoporous materials for production of isopulegol

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Abstract

Cyclization of (+)-citronellal was investigated over zeolites and mesoporous materials as well as on silica under a nitrogen atmosphere in cyclohexane as a solvent. The highest cyclization rates were observed over mesoporous materials and 12-membered ring zeolites with high Brønsted acid concentration, while very low cyclization rates were achieved over silica with low or no Brønsted acidity, respectively. At the same a time low cyclization rate was observed over 10-membered ring pore H-ZSM-5 with a high Brønsted acid site concentration, which is due to diffusional limitation of the product in the narrow pores. The selectivity to cyclization products was very high over all the catalysts, being independent of the conversion of citronellal. Neither concentration of the Brønsted nor Lewis acid sites influenced the stereoselectivity to isopulegol. The support structure had only a minor effect on the stereoselectivity. Quantum mechanical calculations were carried out to explain the experimental results. The calculated stabilities of the carbocationic reaction intermediates correlated well with the observed stereoselectivity. The stereoselectivities were analogous when starting from racemic citronellal mixture or enantiopure (+)-citronellal; the former one gave 8 different pulegols, whereas only 4 pulegols were formed from (+)-citronellal.

Keywords: Mesoporous material; Cyclization; Isopulegol; Acidity

1. Introduction

(−)-Isopulegol is an important intermediate in the production of (−)-menthol [1]. In the cyclization of (+)-citronellal four possible stereoisomers of isopulegol can be formed (Fig. 1). The high stereoselectivity to (−)-isopulegol is needed, because in the commercial production of (−)-menthol, (−)-isopulegol is hydrogenated over nickel catalyst. If the optical purity of (−)-isopulegol is not high enough for the hydrogenation step, it should be improved by a recrystallization step close to 100% [1]. The ene cyclization of (+)-citronellal to (−)-isopulegol proceeds thermally at 180 °C giving 60% stereoselectivity to (−)-isopulegol [2]. The same reaction proceeds over Lewis acids, such as $ZnBr_2$, $AlCl_3$, BF_3, $SbCl_3$ [3], giving high yields and selectivities of the desired product, (−)-isopulegol, i.e., 92 and 94%, respectively. The major drawback of Lewis acid catalysts is the environmentally unfriendly processes [4]. The annual production capacity of (−)-isopulegol from (+)-citronellal with $ZnBr_2$ catalyst by Takasago Co. is about 1100 ton [1]. This process converts (+)-citronellal quantitatively to (−)-isopulegol. Recently a tris(2,6-diarylphenyloxy)aluminium catalyst for the cyclization of (+)-citronellal has been patented by Takasago Co. [5]. This catalyst is able to produce over 95% yield of (−)-isopulegol with stereoselectivities close to 100%.

The use of heterogeneous catalysts can be industrially a more attractive alternative for the production of fine chemicals due to the easy separation and reuse of these catalysts. Moreover, the price of heterogeneous catalysts is generally lower than that of homogeneous complexes. Additionally the use of heterogeneous catalysts allows more environmentally friendly processes than homogeneous catalysts. There exist some publications on the cyclization of (+)-citronellal over heterogeneous catalysts, like zeolites [6], sil-

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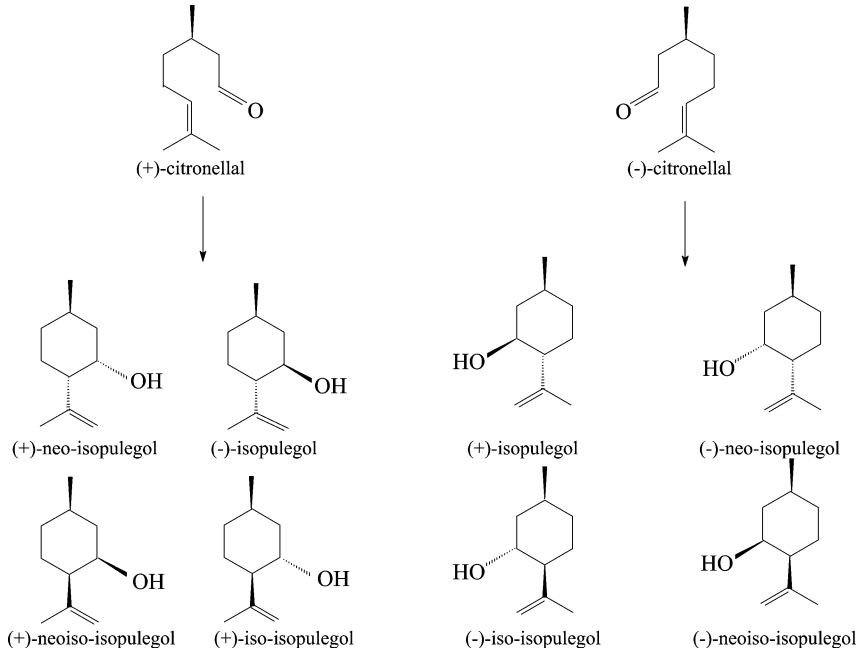

Fig. 1. Reaction scheme.

ica and mixed cogels [2], hydrous zirconia [7], sulfated zirconia [8], supported $ZnBr_2$ [9], and cation-exchanged montmorillonite [10].

Cyclization of citronellal is catalyzed by Lewis [9–12] and Brønsted acid sites [6,7,13]. Lewis acid sites are associated with coordinatively associated unsaturated metal ions [14], whereas Brønsted acidity is related to partially positively charged surface OH groups [15]. Very high yields (98%) and stereoselectivities to (−)-isopulegol (90%) have been obtained over a Zr^{4+}-exchanged montmorillonite catalyst [10], which acts as Lewis acid catalyst in acetonitrile. Additionally it was stated in the work of Ravasio et al. [2] that the stereoselectivity to (−)-isopulegol correlated with the strength of the Lewis acid sites. Al^{3+} is a stronger Lewis acid than Ti^{4+} or Zr^{4+} and the obtained stereoselectivities to (−)-isopulegol over Al_2O_3, SiO_2–TiO_2, and SiO_2–ZrO_2 were 70, 62, and 62% [2]. Another supported Lewis acidic catalyst, $ZnBr_2/SiO_2$, was able to produce maximally 86% stereoselectivities to (−)-isopulegol [9]. It was, however, stated that the catalysts exhibiting residual Zn(II) sites were the most active in the cyclization of (+)-citronellal. The ene cyclization of (+)-citronellal proceeds very fast over sulfated zirconia, but the stereoselectivity toward (−)-isopulegol was maximally 61% [8]. High selectivities to isopulegol (72%) accompanied with high reaction rates were obtained over hydrous zirconia [7]. The low surface area acidic catalysts (i.e., ZrO_2) were also active in cyclization [7]. Moreover, high ene reaction rates were obtained with mixed SiO_2–Al_2O_3 cogels with maximum stereoselectivities about 72% [2]. Interestingly Al_2O_3 has not been active in the cyclization of (+)-citronellal at 58 °C [11]. The difference in the catalytic activity of ZrO_2 [7] and Al_2O_3 [11] can be explained by the difference in the acidic groups. ZrO_2 exhibits both Lewis and Brønsted acidity [7], whereas Al_2O_3 as characterized contains only Lewis acid sites [16]. Very strong acids, like Amberlyst and Nafion favor cracking and etherification reactions. According to Chuah et al. [7] the desired heterogeneous catalysts for the ene cyclization of citronellal should have strong Lewis and weak Brønsted acidity.

Despite the industrial application, the reaction mechanism of citronellal cyclization is under debate. One proposal for the reaction mechanism is the protonation of the carbonyl group of citronellal after which a more stable carbocation is formed via intramolecular rearrangement and the final step is the deprotonation leading to formation of isopulegol [6].

The aim of this paper is to compare in a systematic way different zeolites, mesoporous molecular sieves, as well as silica as catalysts in the cyclization of (+)-citronellal (Fig. 1). The catalyst structure was varied in order to investigate the existence of pore diffusion in the case of zeolites. The particular choice of mesoporous H-MCM-41 was due to its pores, high surface area, and mild acidity. According to the literature, MCM-41 is a potential catalyst for the synthesis of fine chemicals. It has been used, for instance, in the acid-catalyzed acetalization of α-D-glucose [18]. MCM-41 as well as the Ti-modified MCM-41 mesoporous silicate were used in the cyclization of citronellal with high reaction rates and selectivities (98%) [19]. Another material tested in the present study, H-MCM-22 is a new acid catalyst for citronellal cyclization. Moreover, the detailed kinetic analysis of the formation of different pulegol stereoisomers was carried out. According to our knowledge the full kinetic

curves for formation of different products have been reported only in the work of Shieh et al. [13], with, however, profound menthone formation (around 30%) in addition to the cyclization reaction. This result deviates from other cyclization results in the literature [6,7], pointing out that probably the impurities in the raw material, racemic citronellal, affect the product distribution and the cyclization rate. Thus, there is a need to investigate cyclization kinetics in detail. In addition to (+)-citronellal also racemic citronellal was used as a raw material in this work. Molecular modeling was used as a tool to explain the obtained stereoselectivities in pulegols as well as to elucidate the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

Synthesis of the parent form of Na-Beta zeolite was carried out as noted in the literature [20,21]. Ludox AS 40 (Aldrich), sodium aluminate (Riedel de Haen), and tetraethylammonium hydroxide (40% aqueous solution, Fluka) were used as sources of silica, alumina, and organic template, respectively. The gel was prepared by mixing of the above reagents and transferred into a Teflon cup inserted into a stainless-steel autoclave. The autoclave was kept in an oven heated at 150 °C and the synthesis was carried out under static conditions. The products obtained in the synthesis were filtered and washed thoroughly with distilled water. The zeolite was dried at 100 °C and the organic template was removed by heat treatment at 550 °C. The Na-Beta zeolite was transformed to H-Beta by ion exchange with 3 M NH_4Cl solution, followed by drying and calcination at 550 °C.

Synthesis of H-ZSM-5 was carried at 150 °C in an autoclave. The reagents were fumed silica (Aldrich), NaOH (Merck), $Al(OH)_3$ (Aldrich), tetrapropylammonium bromide (Fluka), and distilled water.

The Na-MCM-41 mesoporous molecular sieve was synthesized using the method noted in Refs. [22,23] at 100 °C with tetradecyltrimethylammonium bromide (Aldrich) as a surfactant, sodium silicate solution (Merck) as a source of silica, and sodium aluminate (Riedel Haen) as a source of alumina. The synthesized material was washed thoroughly with distilled water, dried at 100 °C, and calcined in an oven to remove surfactant at 540 °C. The Na-MCM-41 mesoporous material was ion-exchanged with 1 M NH_4Cl solution, washed with distilled water to remove chloride ions, and dried at 100 °C. H-MCM-41 was obtained by calcination of NH_4-MCM-41 in an oven at 530 °C.

Na-MCM-22 zeolite was synthesized as described in Refs. [24,25]. Reagents used in the synthesis of MCM-22 were sodium silicate (Merck), hexamethyleneimine (Aldrich), aluminum sulfate (Merck), distilled water, and sulfuric acid (Merck). Synthesis of the MCM-22 zeolite was carried out in a 300 ml autoclave at 150 °C. Na-MCM-22 product obtained after synthesis was washed with distilled water, dried, and calcined at 550 °C. The H-MCM-22 catalyst was prepared by ion exchange of Na-MCM-22 with 1 M NH_4Cl solution at room temperature for 48 h. NH_4-MCM-22 obtained after ion exchange was dried and calcined at 550 °C for 4 h.

The silica (Merck), alumina (UOP), NH_4-Y (Zeolyst International), and NH_4-mordenite (Zeolyst International) were commercial ones. The ammonium forms of the Y and mordenite were calcined using a muffle oven.

2.2. Catalyst characterization

The characterization of Na-Beta, Na-MCM-41, Na-Beta, and Na-MCM-22 zeolites was carried out using an X-ray powder diffractometer (Philips pW 1800), X-ray fluorescency (Siemens), scanning electron microscope, and a sorptometer (Sorptometer 1900, Carlo Erba Instruments).

The quantitative determination of Brønsted and Lewis acid sites in H-Beta, H-MCM-41, H-MORD, H-Y, H-ZSM-5, H-MCM-22, alumina, and silica catalysts was performed using infrared spectroscopy (ATI Mattson FTIR) with pyridine ($\geqslant$ 99.5%, a.r.) as a probe molecule. The catalysts were pressed into thin wafers (10–12 mg/cm^2) and evacuated at 450 °C for 60 min after which the adsorption of pyridine was carried out at 100 °C for 30 min. The desorption of pyridine was carried out at temperatures 200 °C and spectra recorded at temperature 100 °C with a spectral resolution equal to 2 cm^{-1}. The quantification of the adsorbed pyridine was based on the molar extinction coefficient for pyridine determined by Emeis [26]. The dry catalyst weights were taken into account in calculations.

The surface areas of the fresh catalysts were determined by outgassing the samples at 200 °C for 4 h. The spent catalysts were first dried at 100 °C for 15 h followed by outgassing at 200 °C for 4 h. The Dubinin method was used for calculating the surface area of H-MCM-22, H-Beta, H-Y, H-ZSM-5, and H-MORD. The BET method was applied for calculating the surface area of H-MCM-41, silica, and alumina catalysts.

2.3. Experimental setup

The cyclization of (+)-citronellal (> 99%, Fluka 27478) and citronellal (93%, Acros Organics 40529100) was carried out in an autoclave (V_L = 200 ml) under 10 bar nitrogen (AGA) atmosphere at 90 °C in cyclohexane. The amounts of (+)-citronellal, catalyst and solvent were 200, 200, and 178 g, whereas in the cyclization of racemic citronellal the corresponding amounts were 3 g, 200 mg, and 175 g, respectively. A direct comparison in the cyclization of (+)-citronellal or racemic citronellal was carried out over H-MCM-41 catalyst by using the same initial amounts of either the former or the latter raw material (200 mg). In ad-

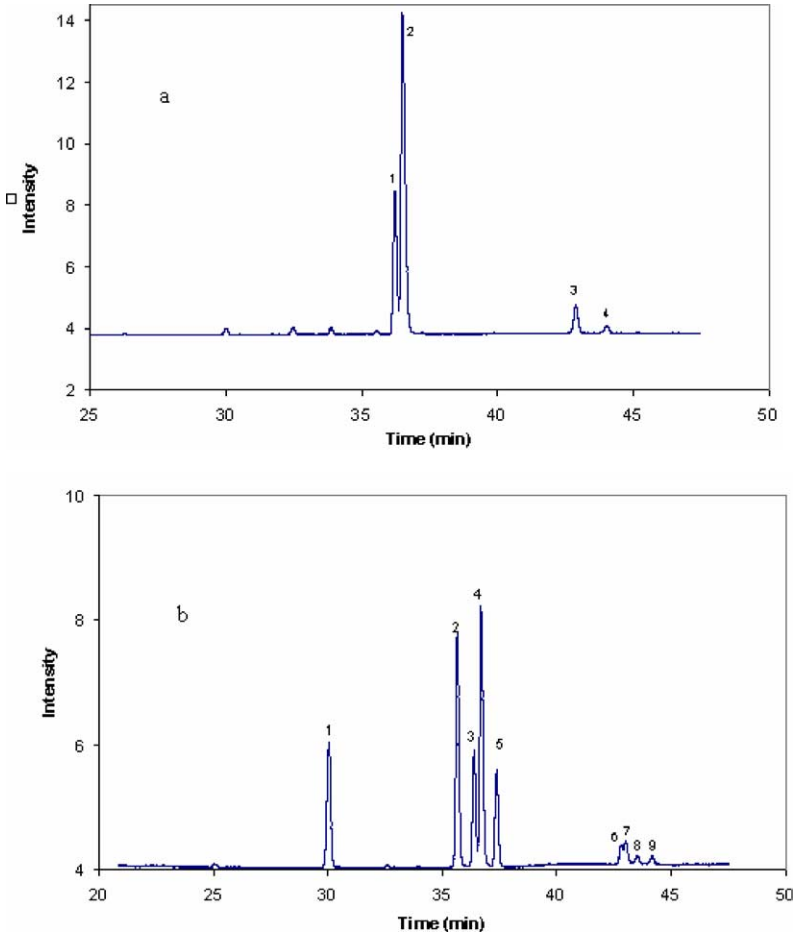

Fig. 2. Gas chromatogram from the separation of different compounds in the reaction mixture in a Cyclodex-B column. Components: (a) 1, (+)-neo-isopulegol; 2, (−)-isopulegol; 3, (+) iso-isopulegol; and 4, (+)-neo-isoisopulegol, (b) 1, citronellal (both enantiomers); 2, (+)-isopulegol; 4, (−)-isopulegol; 3 and 5, two enantiomers of neo-isopulegol; 6 and 7, iso-isopulegol; 8 and 9, neoiso-isopulegol. The enantiomers of citronellal were determined with the β-dex 225 column.

dition, some experiments with (−)-menthone (90%, Aldrich 21823-5) were carried out under the same conditions. The catalysts were sieved and dried at 110 °C and the catalyst particles below 63 μm were used in the experiments in order to avoid mass-transfer limitations. The stirring rate was 1500 rpm. The small size of catalyst particles and efficient stirring assured that the experiments were performed in the kinetic regime [27].

Samples were taken regularly from the reactor and analyzed with a chiral column (Cyclodex-B (Agilent), length 60 m, diameter 0.254 mm, film thickness 0.25 μm). Helium was used as a carrier gas. The products were separated with the following temperature program: 95 °C (1 min), 0.3 °C/min; 120 °C (1 min), 15 °C/min; 220 °C (1 min) with a split of 100:1 (Fig. 2). The detector (FI) and the injector temperature were 280 and 250 °C, respectively. The isomers of the racemic citronellal were separated using a β-dex 225 column (length 30 m, diameter 0.25 mm, film thickness 0.25 μm) and isothermal conditions at 83 °C. The products were quantified by using the following standards: (−)-isopulegol (> 99.5%, Fluka 59770), GC-MS, and ^{1}H NMR analysis (JEOL JNM-LA400 spectrometer) were used in the identification of the samples.

2.4. Molecular modeling

The stabilities of the reaction intermediates, i.e., protonated citronellals, adapting a geometry, which after deprotonation leads to isopulegol, as well as different isopulegol isomers, were evaluated by quantum mechanical calculations. The equilibrium geometries were optimized by the Hartree–Fock (HF) approximation with the 6-31+G** basis set using Gaussian98 software [28]. Frequency calculations were performed to ensure that obtained geometries were energy minima on the potential energy surface. In case of carbocations, single point energies were calculated with second-order Møller–Plesset perturbation theory (MP2). Although extensive conformation analysis was not carried out for the isopulegol isomers and it is possible that the obtained isopulegol conformations are only local but not global minima, although the energy differences between reported values and global minima are presumably rather small. Cerius2 software was used in the illustrations [29].

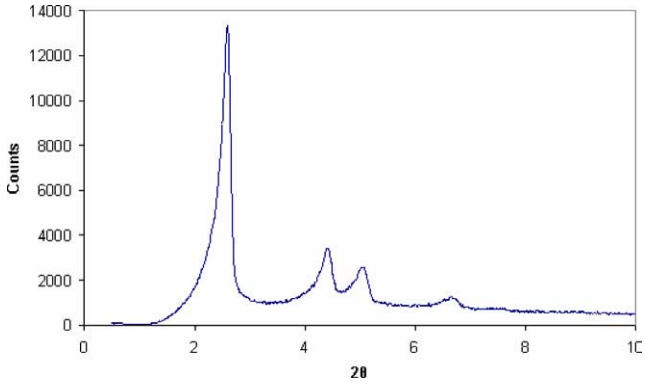

Fig. 3. X-ray powder diffraction pattern of Na-MCM-41.

3. Results and discussion

3.1. Characterization results

The X-ray powder diffraction patterns of Na-Beta, Na-MCM-41, and Na-MCM-22 zeolites synthesized in the laboratory were similar to those reported in the literature. It was inferred from the XRD data that the zeolites synthesized were highly phase pure having structures of that of Beta, MCM-41, and MCM-22. The XRD patterns of Na-MCM-41 and Na-MCM-22 zeolites are given in Figs. 3 and 4.

The specific surface areas of the catalysts measured by nitrogen adsorption are shown in Table 1. The highest specific surface area was observed for H-Y zeolite. The mesoporous H-MCM-41 had the second highest specific surface area, after which the specific surface areas decreased in the following order: H-Beta > H-MORD > H-MCM-22 > H-ZSM-5 > silica > alumina. The spent H-MCM-41 catalyst showed substantial decrease in the surface area after 3 h reaction, indicating pore blockage by organic compounds and coke formation. The catalyst deactivation is discussed in Section 3.2.2.5.

The amount of Brønsted and Lewis acid sites was measured by FTIR with pyridine as a probe molecule. Spectra of Beta zeolite and H-MCM-41 are shown in Fig. 5. The absorption bands of pyridinium ion of adsorbed pyridine corresponding Brønsted acidity is at 1545 cm^{-1}, whereas the adsorbed pyridine is on Lewis acid sites at 1452 cm^{-1}. It should be pointed out that in case of H-MCM-22 and H-Beta two peaks appeared corresponding to Lewis acidity, i.e., the peaks at 1452 and 1448 cm^{-1}.

Table 1
The specific surface areas of different catalysts

Catalyst	Specific surface area of fresh catalyst (m^2/g_{cat})	Specific surface area of spent catalyst[c] (m^2/g_{cat})
H-Beta-11[a,b]	657[d]	433[c]
H-MORD[b]	605[d]	n.m.
H-Y[b]	1218[d]	n.m.
H-ZSM-5[a]	478[d]	n.m
H-MCM-41[a,b]	902[e]	46[c]
H-MCM-22[b]	506[d]	n.m
Alumina[b]	299[e]	n.m
Silica[a,b]	379[e]	358[c]

[a] Cyclization of (+)-citronellal.
[b] Cyclization of racemic citronellal.
[c] After cyclization of racemic citronellal.
[d] Dubinin.
[e] BET isotherm, n.m. not measured.

The amount of Brønsted acid sites decreased in the following order: H-MORD > H-Y ≫ H-MCM-22 > H-Beta ≫ H-MCM-41 ≫ alumina (Table 2). H-MCM-41 has low Brønsted acid site density compared to H-MCM-22 and other zeolites. No Brønsted acidity as expected was observed on silica. The amount of Lewis acidic sites decreased as follows: H-MCM-22 > H-MCM-41 > H-Y > alumina ≫ H-Beta > H-MORD ≫ silica.

3.2. Catalyst testing results

3.2.1. Cyclization of (+)-citronellal

Cyclization of (+)-citronellal was performed over four representative catalysts, namely H-MCM-41, H-Beta,

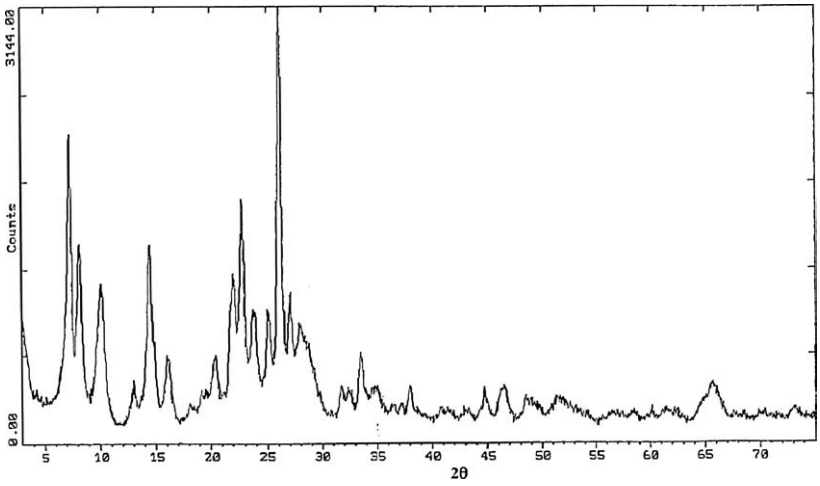

Fig. 4. X-ray powder diffraction pattern of Na-MCM-22.

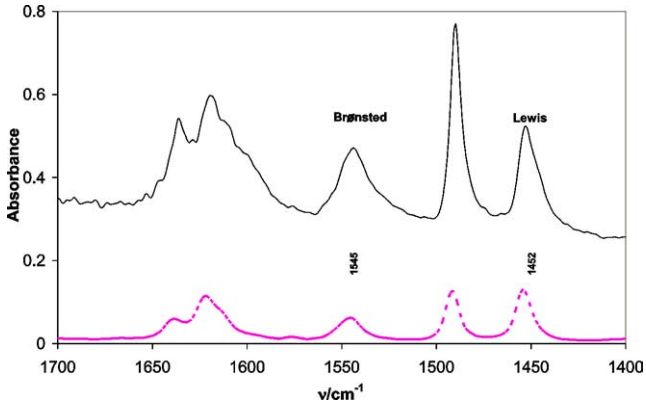

Fig. 5. FTIR spectra of adsorbed pyridine on H-Beta and on H-MCM-41 catalysts. A solid line corresponds to H-Beta and a dashed line to H-MCM-41.

Table 2
Concentration of the Brønsted and Lewis acid sites in different catalysts

Catalyst	Brønsted acid sites (μmol/g_{cat})	Lewis acid sites (μmol/g_{cat})
H-Beta-11	183	128
H-MORD	294	109
H-Y	291	165
H-ZSM-5	374	96
H-MCM-41	89	168
H-MCM-22	187	175
Alumina	7	156
Silica	0	7

Desorption of pyridine carried out at 200 °C.

H-ZSM-5, and silica catalyst, which have large differences in specific surface areas, in concentration of acid sites, as well as in pore sizes. The major products were four stereoisomers of isopulegols formed from (+)-citronellal (Fig. 2a). The maximum selectivity to pulegols was very high over all catalysts (Table 3). This result is in accordance with the work of Ravasio et al. [2], where the selectivity to pulegols was 100% in the cyclization of (+)-citronellal over SiO_2–Al_2O_3 cogel catalyst and SiO_2, Al_2O_3. The detailed results and discussion are given below based on initial cyclization rates, conversion levels, comparison of initial rates and conversion levels, side reactions, and catalyst deactivation as well as from stereoselectivity and product distribution.

3.2.1.1. Initial cyclization rates of (+)-citronellal. The main products were four different pulegols originating from (+)-citronellal (Fig. 2). The amount of other enantiomers of pulegols originating principally from (−)-citronellal was zero or very close to zero. The initial reaction rates decreased in the following order: H-MCM-41 > H-Beta ≫ H-ZSM-5 > silica (Table 3). When comparing the initial reaction rates with the acid site concentrations (Table 2) no correlation was observed. The higher initial rates over H-MCM-41 compared to H-Beta might originate from the pore diffusion over H-Beta catalyst, because H-MCM-41 has larger pores than a zeolite. Very low initial cyclization rates were observed over H-ZSM-5 and silica. Despite the high concentration of Brønsted acid sites in the former catalyst (Table 2), the cyclization rate was low, which indicates the existence of pore diffusion limitations over the H-ZSM-5 having 10-membered zeolite rings. The results from molecular modeling confirmed the problems for isopulegol to penetrate inside H-ZSM-5 (Fig. 10, MFI and FAU correspond to H-ZSM-5 and Y-structures; see Section 3.2.1.4). The same limitations apply for the carbocationic intermediates, which are of the size of corresponding isopulegol isomers. Over silica catalyst, the low initial reaction rate can be explained mainly by the absence of Brønsted acid sites and additionally the low Lewis acid site concentration (Table 2).

It is concluded that the main products were the four isopulegol isomers originating from (+)-citronellal and there was no correlation in the initial cyclization rates and the acid site concentrations. Over H-ZSM-5 catalyst very low initial cyclization rates were observed and these are caused by the diffusion limitations of isopulegols.

3.2.1.2. Conversion levels of (+)-citronellal at prolonged reaction times. The conversion after 3 h reaction time in the cyclization of (+)-citronellal is in the following order: H-Beta-11 ⩾ H-MCM-41 ≫ H-ZSM-5 > SiO_2. The first two catalysts were very active in converting (+)-citronellal, whereas silica and H-ZSM-5 yielded to relatively low conversion levels. Despite the fact that the H-MCM-41 catalyst was more active than H-Beta catalyst (Fig. 6a), the final con-

Table 3
The initial reaction rates and stereoselectivity to (−)-isopulegol, the maximum yield of (−)-isopulegol and the maximum amount of other products formed over different catalysts in the cyclization of (+)-citronellal

Catalyst	Initial reaction rate (mmol/(min g_{cat}))	Conversion after 3 h[a] (%)	Max stereoselectivity to (−)-isopulegol (%)	The total yield of pulegols[a] (%)	Max yield of (−)-isopulegol (%)	Max amount of other products[b] (%)
H-Beta-11	1.8	100	71	95 (75)	71	6
H-ZSM-5	0.04	26	64	25 (64)	16	1
H-MCM-41	6.0	99	67	89 (67)	60	28
Silica	0.03	14	73	100 (73)	13	1

The reaction time was 3 h. Maximum selectivities to pulegols is 100%.
[a] At the stereoselectivity level corresponding to max yield of isopulegols given in parentheses.
[b] The two major products are 4-methyl-1-(2-propyl)cyclohexene and 4-methyl-(1-methylethylidene)cyclohexene.

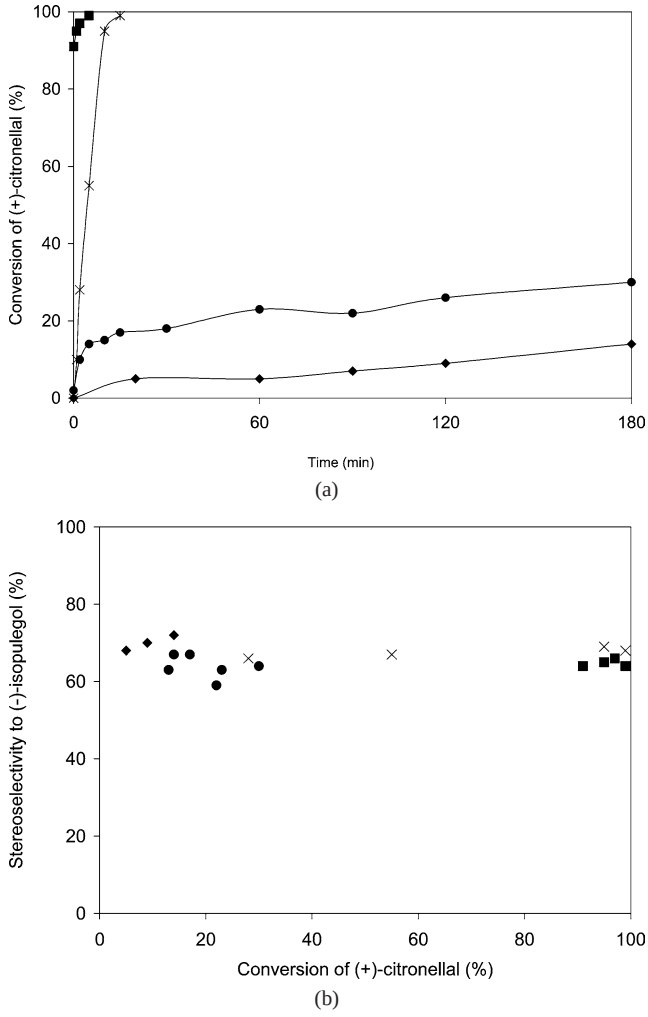

Fig. 6. (a) The conversion of (+)-citronellal and (b) stereoselectivity of (−)-isopulegol as a function of (+)-citronellal conversion at 90 °C in cyclohexane over H-Beta zeolite, H-ZSM-5, silica, and H-MCM-41. Symbols: (■) H-MCM41, (×) H-Beta, (◆) SiO_2 and (●) H-ZSM-5.

version of (+)-citronellal never reached 100%, which was the case over H-Beta (Table 3). Low conversion levels were obtained over silica, exhibiting a very low concentration of acid sites (Table 2). At the same time, conversion was also low over the H-ZSM-5 catalyst, which exhibited high Brønsted acid site concentrations. Pore-diffusion limitations and possible catalyst deactivation can be the reasons for low conversion levels over the H-ZSM-5 catalyst (H-ZSM-5 catalyst exhibits MFI structure; see Fig. 10). Analogous results over H-ZSM-5 catalysts were obtained by Shieh et al. [13], although in that work the starting material was a racemic citronellal.

As a conclusion, it is stated that high conversion levels of (+)-citronellal were achieved over H-Beta and H-MCM-41 catalysts, whereas silica and H-ZSM-5 were not active catalysts in this reaction. The drawback in silica is the low acid site concentrations, whereas the low conversion of (+)-citronellal achieved over H-ZSM-5 is partially due to diffusion limitations over a 10-membered zeolite structure as well as due to the catalyst deactivation.

3.2.1.3. Side reactions in the cyclization of (+)-citronellal. In the cyclization of (+)-citronellal the highest amounts of side products were formed over H-MCM-41 and H-Beta over which very high conversions were achieved. Despite a very high concentration of Brønsted acid sites in the H-ZSM-5 catalyst, only traces of side products were formed, but the conversion level after 3 h over this catalyst remained at 26% (Table 3). The major dehydration products over the H-Beta zeolite and H-MCM-41 were 4-methyl-1-(2-propenyl)cyclohexene and 4-methyl-(1-methylethylidene)cyclohexene confirmed by GC-MS. The formation of dehydration products did not correlate with the catalyst acidity. Besides dehydration products traces of di-isopulegyl ethers, which were formed by the addition of one isopulegol molecule to another one (dimer), were found over the H-MCM-41 catalyst as well as over the H-Beta catalyst with mass numbers 292 and 308, respectively (Fig. 8). The ether formation was observed in the cyclization of racemic citronellal over zeolite catalysts [6].

The main side reactions in the cyclization of (+)-citronellal were dehydration and isomerization. The yield of side products was maximally 28% over H-MCM-41. Additionally traces of di-isopulegyl ethers were observed within the reaction products.

3.2.1.4. Comparison of the initial reaction rates and the conversion levels of (+)-citronellal. In the cyclization of (+)-citronellal there was a decreasing trend in the final conversion with decreasing initial cyclization rate (Table 3). However unexpectedly low final conversions were obtained for (+)-citronellal over H-ZSM-5 (Table 3). This phenomenon can originate from the differences in reaction kinetic over different catalysts as well as from the catalyst deactivation behavior. In the cyclization of (+)-citronellal over H-MCM-41 and H-Beta the initial reaction rates were high and very high conversion levels were obtained. However the cyclization proceeded over H-Beta slightly slower than over H-MCM-41. The reason for this might be the existence of pore-diffusion limitations of organic molecules in the Beta zeolite structure, which has a three-dimensional network of 12-MR pores with diameters of 0.66×0.67 and 0.56×0.56 nm [30]. The low conversion level of (+)-citronellal over the H-ZSM-5 catalyst originates most probably from the diffusional limitations of isopulegol in the structure of H-ZSM-5, which were demonstrated by molecular modeling (Fig. 10, where MFI corresponds to H-ZSM-5). The low intrinsic reaction rates observed over silica resulted in low conversion levels of (+)-citronellal. The illustration of the size of the isopulegol molecule compared to the pore aperture of FAU and MFI structures is given in Fig. 10 (FAU corresponds to Y-zeolite, which was investigated in the cyclization of racemic citronellal). Isopulegol is illustrated by the CPK model, which displays spheres sized to the van der Waals

radii. The pore apertures are illustrated by a Connolly surface. The cavities of the FAU structure are adequate to fit the isopulegol molecule inside, but this is not the case in the MFI structure. The pore wall and hydrogen atoms of isopulegol overlap. Hence, it is reasonable to assume that depending on the pore-size, diffusion of isopulegol can play an inhibiting role in the cyclication reactions of citronellal. It is concluded that the low conversion of enantiopure citronellal over H-ZSM-5 catalyst is due to pore-diffusion limitations of isopulegol as shown by molecular modeling.

As a conclusion it is stated that the most suitable catalysts for cyclization of (+)-citronellal were H-Beta and H-MCM-41, which were able to convert (+)-citronellal totally or close to 100% conversion. Over silica and H-ZSM-5 catalysts relatively low conversion levels were obtained. In the former case the catalyst exhibited a very low acid site concentration, whereas in the latter catalyst the existence of pore diffusion combined with catalyst deactivation yielded to low conversions.

3.2.1.5. Stereoselectivity and product distribution within pulegols. The stereoselectivity of (−)-isopulegol defined as the amounts of (−)-isopulegol divided by the molar amount of all the pulegols was determined by NMR spectroscopy [31]. The stereoselectivity to the desired product, (−)-isopulegol, is around 70% starting from enantiopure citronellal. The major product is (−)-isopulegol and the second major product is (+)-neo-isopulegol following by (+)-iso-isopulegol and (+)-neo-isoisopulegol. The product distribution of pulegols is shown in Table 6. Chuah et al. [7] also reported analogous product distribution of different pulegols compared to this work when starting from either racemic citronellal or (+)-citronellal.

The kinetics of formation of different pulegols has not been previously investigated in detail, only analysis of the product ratio at one point has been reported [7]. In this work, it was possible to separate all the pulegols and thus the formation of different pulegols can be presented as a function of reaction time. The yields of (+)-neo-isopulegol and (−)-isopulegol as well as (−)-iso-isopulegol and (−)-isopulegol are shown in Fig. 7. The formation of (−)-isopulegol isomers correlates with the stabilities of the carbocationic reaction intermediates (Tables 5 and 6). The results indicate the parallel formation of these pulegols. At longer reaction times the stereoselectivities varied over mesoporous catalysts due to side reactions. From the mechanistic point of view it was important to investigate possible interconversion of pulegols, which was additionally investigated with (−)-isopulegol in cyclohexane at 90 °C. Absence of any reactions confirms that there is no interconversion between different pulegols in cyclohexane at the reaction temperature. It is notable, that interconversion between different isomers, i.e., epimerization, requires bond breakage and formation. If epimerization occurs with a low activation energy barrier, the product distribution should be proportional to the stabilities of the isopulegol isomers, resulting in almost 99% of isopulegol. This was not observed. The linear ratio between the yields of (+)-neo-isopulegol and (−)-isopulegol, defined as $\alpha = y_{NIP}/y_{IP}$, gave the value for $\alpha = 0.4$, whereas the corresponding value for β giving the ratio between the yields of (−)-iso-isopulegol and (−)-isopulegol, defined as $\beta = y_{IIP}/y_{IP}$ was 0.1.

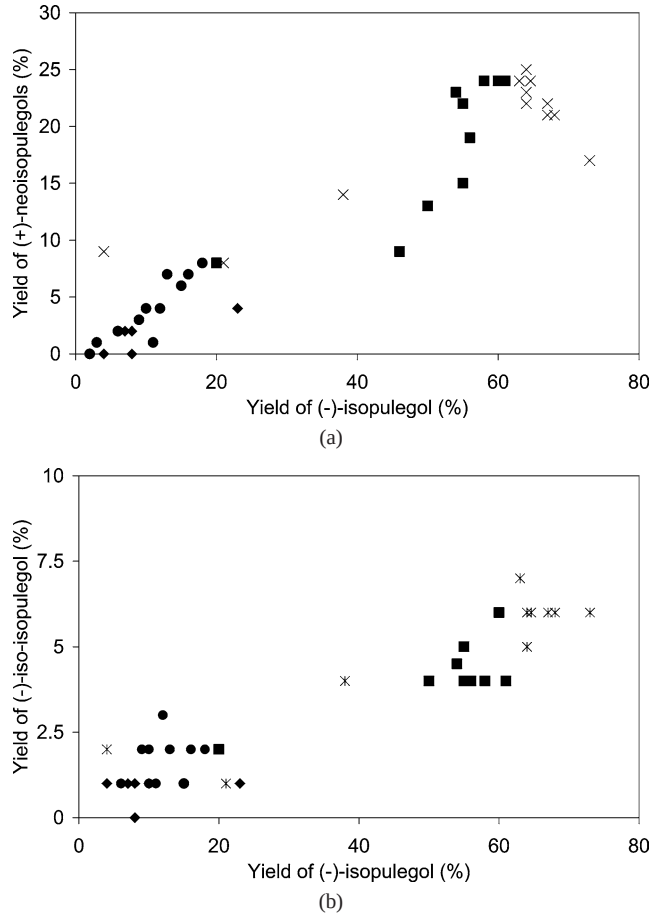

Fig. 7. The yield of (a) neo-isopulegol and (b) iso-isopulegol as a function of (−)-isopulegol over different catalysts in the cyclization of (+)-citronellal. Symbols: (■) H-MCM41, (×) H-Beta, (◆) SiO_2 and (●) H-ZSM-5.

Table 4
The relative energies of the isopulegol isomers calculated by optimized structures

Molecule	Energy in kJ/mol
eee-isopulegol	0
aaa-isopulegol	42
eae-neo-isopulegol	15
aea-neo-isopulegol	38
eea-iso-isopulegol	19
aae-iso-isopulegol	23
aee-neoiso-isopulegol	31
eaa-neoiso-isopulegol	17

For each isomer two different conformations are concerned. Letters *a* and *e* indicate axial or equatorial position of the substituent in the cyclohexane ring in the following order: isopropylene, hydroxy, and methyl. Cyclohexane ring has chair conformation in all cases.

Table 5
Relative energies (HF/6-31+G**//HF/6-31+G**/MP2) and Bolzmann distribution of the carbocationic intermediates, i.e., protonated isopulegols (see Fig. 9), which after deprotonation lead to corresponding pulegol isomers

	Relative energy (kJ/mol)	Bolzmann distribution
Protonated eee-isopulegol	0.0	0.77
Protonated eae-neo-isopulegol	5.0	0.15
Protonated eea-iso-isopulegol	7.1	0.07
Protonated eaa-neo-iso-isopulegol	14.5	0.01

Table 6
The stereoselectivity ratio for different pulegols at given conversion level in the cyclization of (+)-citronellal

Catalyst	Ratio of y_{IP}:y_{NIP}:y_{IIP}:y_{NIIP} (%)
H-Beta-11	68:27:5:1[a]
H-ZSM-5	67:22:11:0[b]
H-MCM-41	64:27:7:2[a]
Silica	67:27:7:2[b]

[a] 95% conversion level.
[b] 10% conversion level.

The relative stabilities of the different isopulegol isomers are given in Tables 4 and 5. All isomers were supposed to adopt a chair conformation and thus, two conformations have been optimized for each isomer. Isopulegol conformation, in which all substituents of the cyclohexane ring are in equatorial position, is about 15 kJ/mol more stable than the other three isopulegol isomers, each of them in the most stable conformation. This is understandable, since substituents in equatorial position possess less steric hindrance compared to substituents in the axial position. Only isopulegol can adopt a conformation, in which all substituents are in equatorial position. The most stable conformations of the other isomers are almost equal in energy.

The reaction scheme of isopulegol formation by the protonation of citronellal is given in Fig. 9. Protonation of citronellal by Brønsted acid leads to a protonated citronellal. These species are readily transferred into "more stable carbocations" by intramolecular rearrangement (i.e., cyclization in this case), as proposed by Fuentes et al. [6]. The formed carbocations have the same structure as the four possible isopulegol stereoisomers and the deprotonation of each carbocationic species leads to a corresponding isopulegol isomer. Thus, the reaction intermediate species are named as "protonated isopulegols," although they are formed from

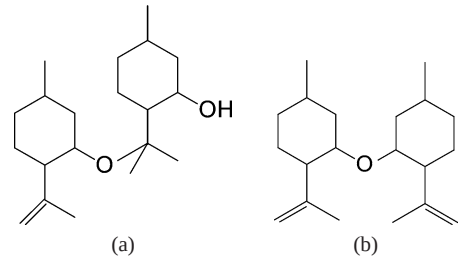

Fig. 8. Di-isopulegyl ethers with mass (a) 308 and (b) 292 formed over H-MCM-41.

citronellal. The relative stabilities of these protonated isopulegol intermediates are given in the Table 5. The Bolzmann distribution of the protonated isopulegols, which is proportional to the presence of each protonated isopulegol intermediate species in the reaction mixture, is given in Table 5 as well. It is notable that in the table it is assumed that only these four species exist; however, this is not the case in reality. An evident correlation exists between stereoselectivity and distribution of the reaction intermediates (Tables 3, 5, and 6). These results suggest that stereoselectivity to different isopulegol isomers is based on the stability of the carbocationic reaction intermediates (protonated isopulegols) leading to a corresponding stereoisomer (isopulegol). However, these calculations overestimate the proportion of the isopulegol isomer and underestimate the proportion of other isomers, respectively.

It can be concluded that the stereoselectivity to (−)-isopulegol was independent of the concentration of Brønsted and Lewis acid sites as well as on the specific surface area of the catalyst. Additionally stereoselectivity was constant during (+)-citronellal conversion. The main stereoisomer was (−)-isopulegol followed by (+)-neoisopulegol, (+)-iso-isopulegol, and (+)-neo-isopulegol. There was no interconversion between different pulegols and from a mechanistic point of view it can concluded that different pulegols are formed in parallel. The carbocation stabilities of the reaction intermediate correlated with the observed stereoselectivity ratio.

3.2.2. Cyclization of racemic citronellal

3.2.2.1. Qualitative kinetics. Cyclization of racemic citronellal was carried out over seven different catalysts (Table 1). The main products were four enantiomer pairs of different pulegols, when starting from racemic citronel-

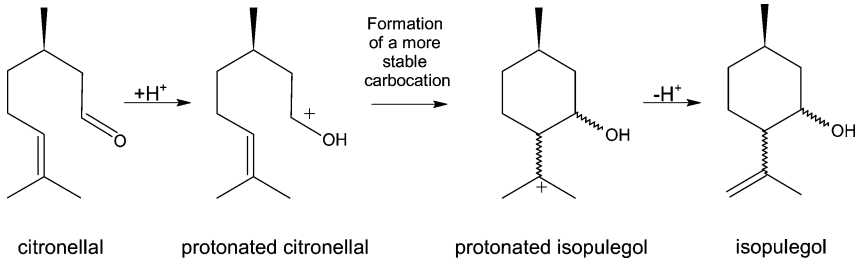

Fig. 9. Reaction scheme for isopulegol formation via carbenium ion intermediates.

Table 7
The initial reaction rates, conversion levels, and maximum selectivities to isopulegol starting from different reactant and different initial concentrations of racemic citronellal over H-MCM-41 catalyst

Reactant	Initial concentration of reactant (M)	Initial reaction rate (mmol/(min g_{cat}))	Conversion after 3 h (%)	Max stereoselectivity to isopulegol (%)
Racemic citronellal	0.0065	0.7[a]	100	70[b]
Racemic citronellal	0.1	22[a]	97	68[b]
(+)-Citronellal	0.0065	6.0	99	67[c]

[a] The starting material, racemic citronellal, contained initially 8 mol% isopulegols and the conversion level was calculated from the formed products.
[b] (±)-isopulegol.
[c] (−)-isopulegol.

Table 8
The initial reaction rates and the maximum selectivities to (±)-isopulegol, the maximum yield of isopulegol and the maximum amount of other products formed over different catalysts in the cyclization of racemic citronellal. Maximum selectivities to pulegols is 100%

Catalyst	Initial reaction rate (mmol/(min g_{cat}))	Conversion after 3 h (%)[a]	Max stereoselectivity to (±)-isopulegol (%)	The total yield of pulegols (%)[b]	Max yield of isopulegol (%)	Max amount of other products after 3 h (%)[d]
H-Beta-11	3.5	71	72	69 (66)	48	1
H-MORD	4.3	85	67	76 (63)	48	10
H-Y	7.0	98	67	95 (65)	62	3
H-MCM-41	22	97	68	94 (68)	64	21
H-MCM-22	19	100	67	82 (67)	55	18
Alumina	0.03	10	72	17 (72)	12[c]	0
Silica	0.05	5	72	10 (70)	7[c]	2

[a] The starting material, racemic citronellal, contained initially 8 mol% isopulegols and the conversion level was calculated from the formed products.
[b] At the stereoselectivity level corresponding to max yield of isopulegols given in parentheses, whereas the pulegols yields include both initial amounts as well as the formed amounts of pulegols.
[c] Thus the yields can be larger than the total conversion.
[d] The two major products are 4-methyl-1-(2-propyl)cyclohexene and 4-methyl-(1-methylethylidene)cyclohexene.

lal (Fig. 2b). The catalyst screening in the cyclization of racemic citronellal was affordable to perform with the initial citronellal concentration of 0.1 M. Before starting the catalyst screening a direct comparison between the cyclization of (+)-citronellal and racemic citronellal was, however, carried out with the same initial concentrations of reactants (0.0065 M) over H-MCM-41 catalysts. The results from the comparison of the cyclization from (+)-citronellal and racemic citronellal are shown in Table 7. It can be seen from Table 7 that the initial cyclization rates over racemic citronellal were about 8.6 times lower than starting from (+)-citronellal. The difference in the initial rates most probably originated from the presence of racemic citronellal of other than pulegols impurities. This reasoning is based on the experimental data that isopulegols were not limiting the cyclization rate over different catalysts. The maximum stereoselectivities to either (±)-isopulegols or (−)-isopulegol were not, however, affected by starting from racemic or (+)-citronellal. Additionally the initial cyclization rate of racemic citronellal was increased by factor 31 when the initial reactant concentration was increased 15-fold (Table 7), which indicated weak adsorption of citronellal on the catalyst surface.

The selectivities to pulegols were very high over H-Beta, H-Y, alumina, and silica catalysts, whereas dehydration and isomerization reactions took place to a larger extent over H-MORD, H-MCM-41, and H-MCM-22 (Table 8, Section 3.2.2.4). Lower selectivities to pulegols have been reported in the cyclization of racemic citronellal over zeolites and MCM-41 catalysts, where the major by-product was menthone (30%), formed over MCM-41 and two types of zeolites, H-ZSM-5 and H-Beta as well as over Al-MCM-41 [13]. According to GC-MS analysis, no menthone was formed in this work. Experiments in the present study have been carried out under vigorous stirring in cyclohexane under nitrogen at 90 °C, while the data of Shieh et al. [13] were acquired in a glass reactor at 60 °C in toluene under air and the raw material contained, in addition to citronellal, also 8.6% of impurities. Additionally the reaction of menthone was investigated in the present work under the same reaction conditions over β-zeolite and no reaction was observed.

The major products in the cyclization of racemic citronellal were 8 isomers of citronellal and no menthone formation was observed. High selectivities to cyclization were observed over H-Beta, H-Y, silica, and alumina, whereas more side reactions occurred over H-MORD, H-MCM-41, and H-MCM-22.

3.2.2.2. Initial cyclization rates of racemic citronellal. The initial cyclization rate of racemic citronellal was about 3 times higher over mesoporous catalyst and H-MCM-22 than over the most active zeolite, H-Y (Table 8). Interestingly it can be seen that the presence of 12-membered rings in H-MCM-22, which also has 10-membered rings, is enough for

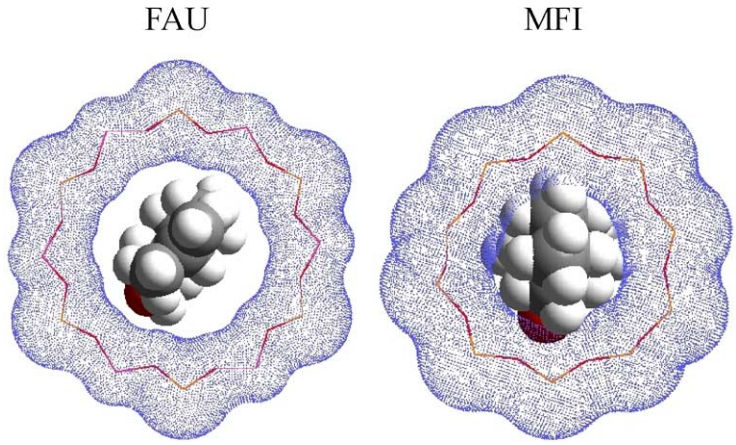

Fig. 10. Image of the isopulegol molecule inside the pores of FAU and MFI structures. Isopulegol is illustrated by the CPK model, which displays spheres sized to the van der Waals radii. The pore apertures are illustrated by a Connolly surface.

catalyzing the cyclization of citronellal. Two other zeolite catalysts, H-Beta and H-MORD, exhibited half the reaction rate of H-Y. Very low cyclization rates were observed over Al_2O_3 and SiO_2 catalysts. Analogous results with low catalytic activity of SiO_2 in the cyclization of citronellal were reported by Chuah et al. [7]. The low activity of silica is due to the lack of Brønsted acid sites. The importance of Brønsted acidity was demonstrated in the work of Kropp et al. [17], where silica gel was used as a catalyst in the cyclization of citronellal and the addition of adsorbed phosphoric acid enhanced the cyclization rate of citronellal. The Al_2O_3 catalyst used in this work had very low Brønsted acid site density, which indicates that Lewis acidity alone is not enough to achieve high reaction rates. The initial cyclization rates over H-MCM-41 and H-MCM-22 were high compared to the rates obtained over H-Beta, H-Y, and H-MORD, which had high concentration of Brønsted acid site. The reason for apparently high activity can partially be the lack of diffusion limitations of organic molecules, when using the former catalysts.

The low initial cyclization rates over silica and alumina are clearly due to low concentrations of Brønsted acid sites. As a comparison, no catalytic activity was observed in the cyclization of (+)-citronellal over alumina and silica at 58 °C [11]. As noted above the high initial reaction rates could be obtained over catalysts having large specific surface areas, like H-MCM-41 and HMCM-22. One exception was, however, H-Y, which exhibited the highest specific surface area, but the initial reaction rate was relatively low. Although the results of molecular modeling show that isopulegol fits inside Y-zeolite structure (Fig. 10, FAU) the presence of pore-diffusion limitations cannot be excluded. The pore of FAU consists of a circular 12-ring channel with a window diameter of 0.74 nm connecting almost spherical 1.18 nm cavities (supercages) [30]. In the previous study of Fuentes et al. [6] on the cyclization of citronellal the correlation between activity and acidity was also noted. However in Ref. [6] the acidity was measured by ammonia adsorption, which was accessible to investigated zeolites, while with citronellal and/or isopulegol diffusional limitations might exist due to their dimensions. Additionally it should be pointed out that pyridine, which was used in this work as a probe molecule in acidity measurements, is sterically a more representative molecule than ammonia.

It can be concluded that high initial reaction rates can be achieved with the catalysts having large pores and enough Brønsted acid sites to catalyze citronellal cyclization.

3.2.2.3. Conversion levels of racemic citronellal. The conversion of citronellal using racemic citronellal was calculated taking into account the initial amount of isopulegols (8%) in citronellal (Table 8, Fig. 11a). The conversion of citronellal after 3 h reaction decreased in the following order: H-MCM-22 > H-Y > H-MCM-41 ≫ H-MORD > H-Beta-11 ≫ Al_2O_3 > SiO_2. Very low conversions over Al_2O_3 and SiO_2 can be explained by the low concentration of Brønsted acid sites, but with other catalysts there was no correlation between the catalyst acidity and the final conversion level. Moreover, the final conversion was not correlating with the specific area of the catalyst. The difference of activities over Beta zeolite when using racemic citronellal or (+)-citronellal might be due to the reactant purity; i.e., (+)-citronellal was more pure than racemic citronellal. The main impurities in the racemic citronellal were isopulegols according to GC-MS analysis. Isopulegols are from a catalytic point of view reaction products. The trace amounts of other impurities remained unidentified. The difference in the final conversion level in the cyclization of either (+)-citronellal or racemic citronellal is, however, not due to the presence of pulegols, because very high conversion of (+)-citronellal was obtained over H-Beta catalysts. An explanation is that the other impurities than pulegols in racemic citronellal might deactivate the H-Beta catalysts. Comparison of the catalytic performance of the H-Beta catalyst revealed that it is dangerous to draw any conclusions regarding the

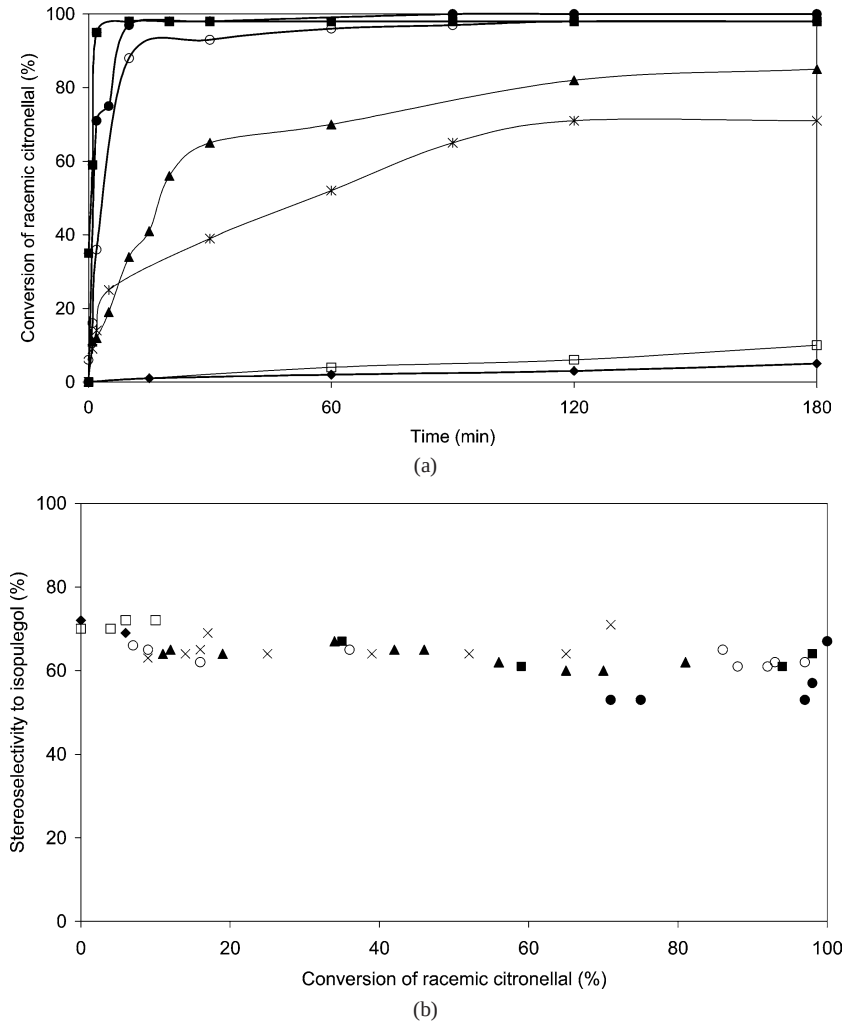

Fig. 11. (a) Conversion of citronellal and (b) stereoselectivity of isopulegols as a function of citronellal conversion at 90 °C in cyclohexane over different catalysts. Symbols: (■) H-MCM41, (×) H-Beta, (○) H-Y, (●) H-MCM-22, (▲) H-MORD, (□) Al_2O_3 and (◆) SiO_2.

reaction mechanism, when starting from racemic citronellal and not taking into account deactivation because the trace amounts of impurities can cause large differences in the final conversion level. Although in the work of Chuah et al. [7] it was reported that comparable results were obtained in the cyclization of (+)-citronellal and racemic citronellal, it is not the case in the present study. Over H-MORD the final conversion was also relatively low, comparable to that obtained over beta zeolites. The origin of the low conversion level over H-MORD can be either pore-diffusion limitations of isopulegols or impurities in racemic citronellal, similarly to H-Beta. High catalytic activity of H-Y compared to H-MORD cannot be explained in terms of pore diffusion, as according to molecular modeling isopulegol can penetrate through the pores in H-Y (Fig. 10).

As a conclusion, it can be stated that the achieved final conversion levels of racemic citronellal over different catalysts can be affected by several factors, like impurities in the reactant, the catalyst deactivation, and the pore diffusion over zeolites. Additionally this work revealed that it is dangerous to draw any conclusions from the reaction mechanism based exclusively on the experimental results from racemic citronellal.

3.2.2.4. Side reactions in the cyclization of racemic citronellal. The formation of other than cyclization products was minor over H-Beta, SiO_2, and Al_2O_3 catalysts, while over H-MORD around 10% of other products were formed (Table 8). Over a mesoporous catalyst ca. 20% of other products were obtained after 3 h, mainly due to dehydration. Over the H-MORD quite large amounts of dehydration products were formed and simultaneously the catalyst was deactivated, because only a 85% conversion level was achieved, whereas over the H-Y catalyst the achieved conversion level was 98% and only 3% dehydration products were formed (Table 8). Over mesoporous materials the larger cavities can favor formation of by-products. Traces of di-isopulegyl ethers were also observed in the product mixture starting from racemic citronellal. Fuentes et al. [6] have also observed the formation of isopulegyl ethers over zeolite catalysts.

Table 9
The stereoselectivity ratio for different pulegols at given conversion levels in the cyclization of racemic citronellal

Catalyst	Ratio of y_{IP}:y_{NIP}:y_{IIP}:y_{NIIP} (%)	Ratio of y_{IP}:y_{NIP}:y_{IIP}:y_{NIIP} (%)[c]
H-Beta-11	67:29:3:1[a]	69:27:3:1[a]
H-MORD	60:31:6:3[a]	61:30:6:2[a]
H-Y	62:29:5:4[a]	61:29:5:5[a]
H-MCM-41	62:31:5:2[a]	60:33:4:3[a]
H-MCM-22	52:27:17:4[a]	52:26:18:3[a]
Alumina	70:26:4:0[b]	75:15:10[b]
Silica	72:24:4:0[b]	77:19:4[b]

[a] Conversion level 0.7.
[b] Conversion level 0.05.
[c] Corrected with the initial amount of isopulegols in racemic citronellal.

It can be concluded that larger amounts of side products were formed over H-MCM-41 and H-MCM-22 catalysts than over zeolites, alumina, and silica.

3.2.2.5. Catalyst deactivation in the cyclization of racemic citronellal. Catalyst deactivation normally occurs when organic molecules are contacted with acidic catalysts. Especially coke can be formed inside the pores, which can lower the conversion level and affect the product selectivity. One of the methods to investigate catalyst deactivation is to measure the specific surface areas of the spent catalysts and compare these values with the specific surface areas of the fresh catalyst. This comparison was carried out for H-MCM-41, Beta zeolite, as well as for silica (Table 1). It should be pointed out here that in some cases the cyclization was very fast, like over H-MCM-41, and the side reactions occurring after citronellal conversion can form coke on the catalyst surface. The specific surface areas of the spent catalysts confirmed the accumulation of organic compounds inside the H-MCM-41 catalysts, whereas in case of silica the specific surface area decreased only slightly (Table 1). It should be pointed out that despite the large decrease of the catalyst specific surface area, the H-MCM-41 structure was, however, intact during the reaction, similarly to liquid-phase isomerization of linoleic acid over Ni-H-MCM-41, where the used catalyst revealed the typical XRD pattern of H-MCM-41 [32]. Large amounts of organic material were accumulated inside the H-MCM-41 catalysts, whereas the situation was different over the H-Beta catalyst. The specific surface area of H-Beta decreased during the reaction by about 34% (Table 1) and a relatively low conversion level of racemic citronellal was achieved (71%, Table 8). This can be partially explained by the quite large accumulation of organic compounds inside the smaller catalyst cavities in β-zeolite compared to H-MCM-41. After only 5 min reaction time the catalyst deactivation in the cyclization of racemic citronellal was very prominent for H-Beta and H-MORD, but unexpectedly not for H-Y (Fig. 11a). The H-MORD structure consists of straight 12-MR with diameters of 0.70×0.65 nm connected by short alternating 8-MR channels with diameters of 0.57×0.26 nm [30]. Interestingly the conversion level of (+)-citronellal over beta zeolite was 100%, indicating that the impurities other than isopulegols in racemic citronellal caused the catalyst deactivation.

It can be concluded that catalyst deactivation was the most prominent for H-Beta and H-MORD catalysts, over which the final conversion of racemic citronellal was 85 and 71%, respectively. Despite the large decrease in the specific surface area in the spent H-MCM-41 catalyst it still exhibited high catalytic activity leading to nearly full conversion of citronellal. The differences in catalytic performances of H-Beta starting from racemic and enantio pure citronellal originated from the differences in catalyst deactivation, but not from the presence of pulegols in racemic citronellal.

3.2.2.6. Stereoselectivity in the cyclization of racemic citronellal. The stereoselectivity of (±)-isopulegols defined as the sum of the amounts of (+)-isopulegol and (−)-isopulegol divided by the molar amount of all the pulegols was determined by NMR spectroscopy [31]. When comparing the product distribution of pulegols it can be seen that at the 70% conversion the most selective catalysts have been H-Beta, H-MCM-41, H-Y, and H-MORD, whereas lower stereoselectivities for (±)-isopulegols were obtained over H-MCM-22 catalyst (Table 9, Fig. 11b), which has very prominent formation of iso-isopulegol. This result contradicts the data of Chuah et al. [7], who concluded that the stereoselectivity was unaffected by the pore structure of the catalyst. The stereoselectivity in pulegols changed over H-MCM-41, when the reaction was continued after the full conversion of citronellal and about 20% of dehydration and isomerization products, like 4-methyl-1-(2-propyl)cyclohexane (Table 8), were formed. Additionally, silica and alumina catalysts gave quite high stereoselectivities but the yields of (±)-isopulegols were very low. The highest yields of isopulegols were obtained over H-Y and H-MCM-41, being 62 and 64%, respectively (Table 8). These catalysts were also very active and had very high specific surface area (Table 1). No symmetry breaking was observed and cyclization of racemic citronellal resulted in racemic pulegols. The stereoselectivities to isopulegol starting from racemic citronellal varied in the range of 60–72% (Table 7, Fig. 11b). Only with the H-MCM-22 catalyst the stereoselectivities were somewhat

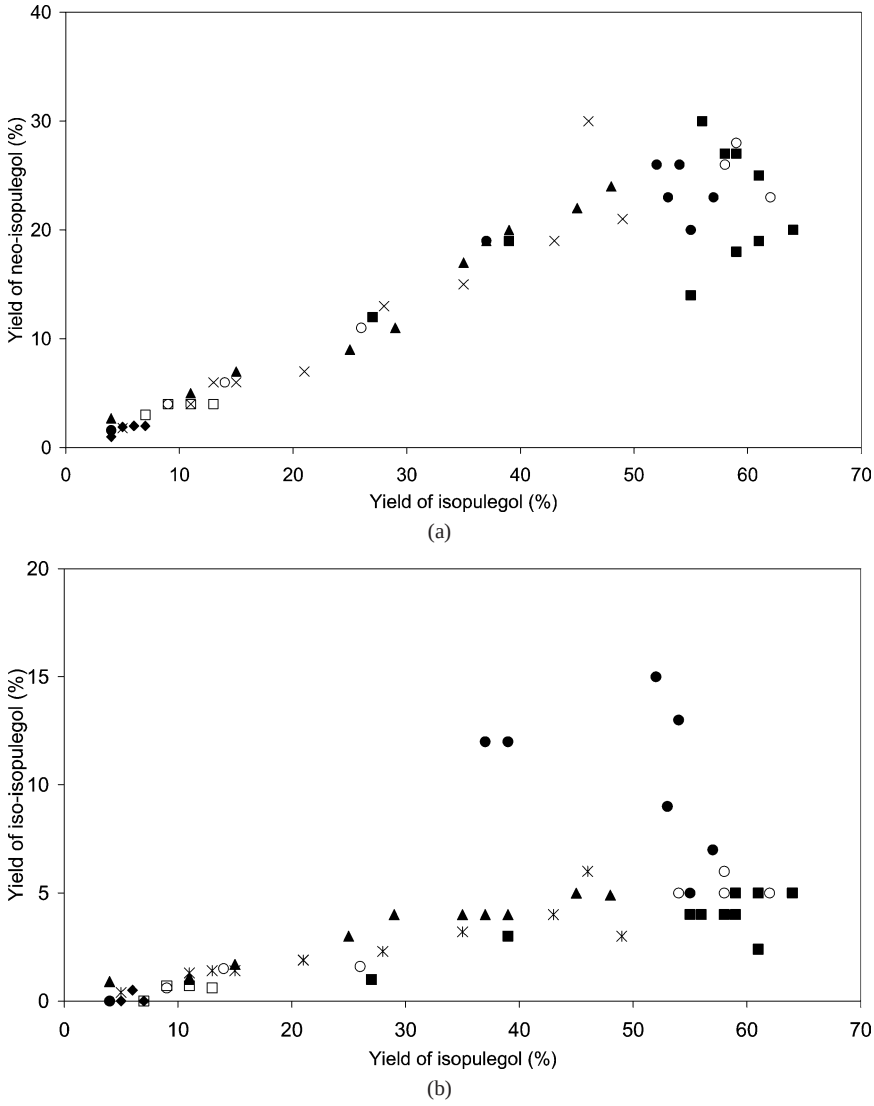

Fig. 12. The yield of (a) neo-isopulegol and (b) iso-isopulegol as a function of the yield of isopulegol over different catalysts. Symbols: (■) H-MCM41, (×) H-Beta, (○) H-Y, (●) H-MCM-22, (▲) H-MORD, (□) Al_2O_3 and (◆) SiO_2.

lower than with other catalysts (Fig. 11b). Moreover the stereoselectivities were constant with the increasing conversion of citronellal and independent of the concentration of acid sites (Fig. 12). In the work of Ravasio et al. [2] the stereoselectivity to (−)-isopulegol varied, however, in the quite narrow range of 62 to 72%. Additionally it was concluded in their work that the strong Lewis acidic catalysts can increase the stereoselectivity of (−)-isopulegol.

It can be concluded in this work that there was no correlation between with the concentration of acid sites and the obtained stereoselectivities. Additionally stereoselectivities were independent of the conversion of citronellal.

4. Conclusions

Cyclization of (+)-citronellal was investigated over zeolites and mesoporous materials as well as on silica under a nitrogen atmosphere in cyclohexane as a solvent. The high initial rates in cyclization of (+)-citronellal were observed for catalysts which exhibited high enough concentration of Brønsted acid sites. One exception was the H-ZSM-5 catalyst, which showed relatively low catalytic activity and a low conversion level compared to the concentration of the acid sites. The origin of low initial cyclization rates of (+)-citronellal was pore-diffusion limitations of isopulegol over 10-membered zeolite catalysts, although the catalyst deactivation cannot be excluded. The presence of pore-diffusion limitations is also supported by molecular modeling, which indicated that the isopulegol molecule is too large to diffuse efficiently into the cavities of H-ZSM-5. The results indicate that over zeolites the pore-diffusion limitations of isopulegol could not be excluded, pointing out that there is no direct correlation among the initial cyclization rates, the specific surface areas, and the concentration of acid sites.

The total selectivity to pulegols was very high over all the catalysts being close to 100%, independent of the conversion of citronellal. The stereoselectivity to isopulegols varyed between 55 and 72%, but no correlation between the stereoselectivity and the concentration of acid sites was seen. From a mechanistic point of view, it can be concluded that the formation of different isopulegols was parallel; i.e., no interconversion between different pulegols occurs. Additionally the stability of the reaction intermediates obtained by quantum mechanical calculations correlated reasonable well with the obtained stereoselectivities in the cyclization of citronellal.

In the cyclization of racemic citronellal very high cyclization rates were observed over H-MCM-41 and H-MCM-22, whereas the catalyst exhibiting the highest specific surface area and high concentration of acid sites, namely H-Y catalyst, converted citronellal with a lower initial rate than the former ones. Comparison of the initial cyclization rates and the final conversion level of citronellal indicated that the catalyst was deactivated over H-MORD and Beta zeolite in the cyclization of racemic citronellal. In the case of Beta zeolite the final conversion varied very much when starting from either enantio-pure citronellal or racemic citronellal. In the former case very high conversions were obtained. These results demonstrate that isopulegol in the feed is not the inhibiting factor in the cyclization of racemic citronellal, but it must be the other impurities in racemic citronellal. In the case of H-MORD the low conversions can originate either from pore-diffusion limitations of isopulegol or due to deactivation from the impurities in racemic citronellal. These results indicate that it is dangerous to draw mechanistic conclusions from the kinetics in the cyclization of racemic citronellal without taking into account deactivation. Stereoselectivity was constant during the conversion of citronellal, after which side reactions, like dehydration and hydrogenolysis, occurred, mostly over H-MCM-41 and H-MCM-22.

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