

# One-pot citral transformation to menthol over bifunctional micro- and mesoporous metal modified catalysts: Effect of catalyst support and metal

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## Abstract

Citral transformation to menthols was conducted in liquid phase over Ni supported H-MCM-41 and H-Y. The highest selectivity to four different stereoisomers of menthol and to (±)-menthols over Ni-H-MCM-41 were 54 and 38%, respectively. The effect of different metals (Ni, Ir, Ru, Pd) was studied over H-MCM-41. The selectivity to menthols decreased in the following order: Ni > Pd > Ru > Ir.

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**Keywords:** Ni-H-MCM-41; Citral; Menthol; Bifunctional catalyst

## 1. Introduction

Menthol is an industrially important product used as a flavor and a pharmaceutical and in oral care [1]. (–)-Menthol can be isolated directly from natural sources, produced via semi-synthetic routes which involve separation from racemates or directly via asymmetric synthesis. In 1998 the share of synthetic (–)-menthol was 20% from the total world market being 2500 t [2]. There exist four different stereoisomers of menthols, namely (±)-menthols, (±)-neomenthols, (±)-isomenthols and (±)-neoisomenthols. Additionally each of them consists of pairs of enantiomers. Menthol is industrially produced via a two-step process, i.e. cyclisation of (+)-citronellal followed by hydrogenation of (–)-isopulegol to (–)-menthol. In the cyclisation of (+)-citronellal over an acid catalyst about 70–80% (–)-isopulegol is obtained as a product, whereas the rest consists of racemates [3]. Several acid

catalysts have been investigated in the cyclisation of citronellal, like zeolites [4,5], mesoporous materials [4], zirconia [6]. In the industrial process (–)-isopulegol is crystallized before hydrogenation in order to get a menthol mixture from which (–)-menthol is separated. Racemic menthols can be produced via catalytic hydrogenation of thymol [7] and mixtures of neomenthol, isomenthol and neoisomenthol can be isomerized over heterogeneous catalyst to produce about 65% racemic menthols [7,8]. Enantiopure (–)-menthol can be produced via several different methods. One method is to start from myrcene using a homogeneous Rh BINAP catalyst in the transformation of diethylgeranylamine to *R*-citronellal enamine [9]. Other methods reported in recent patent literature are following: via using a three step homogeneously catalyzed hydrogenations of piperitenone to pulegone followed by its hydrogenation to pulegol and finally to menthol [10], as well as hydrolysis of menthyl esters with enzymes [11] and biological hydroxylation of natural compounds, like 4*R*-(+)-menthene or 4*R*-(+)-limonene to *trans*-piperitol and its hydrogenation over heterogeneous catalysts to menthols [12].

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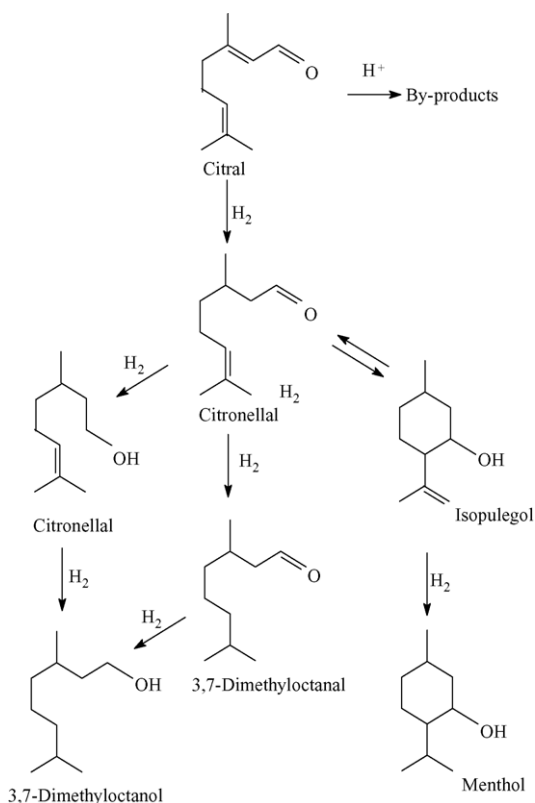


Fig. 1. Reaction scheme for transformation of citral to menthols.

One-pot synthesis of menthol starting from citronellal has been investigated recently over Ru/SiO<sub>2</sub> [13] and over Ir/Beta [14]. In the former case about 80% menthols were obtained at 60 °C under atmospheric pressure in cyclohexane. In the latter work maximally 84% selectivity to menthols was obtained over 5% Ir/Beta catalyst in cyclohexane at 80 °C under atmospheric pressure.

One-pot synthesis of menthol directly from citral can, however, be a difficult task, because it includes selective hydrogenation of citral to citronellal followed by its cyclisation and hydrogenation of (–)-isopulegol to menthol (Fig. 1). Additionally there are four different pulegols and menthols, which can be formed in the reaction (Fig. 2). All of them exist as pairs of enantiomers. There exists only one research note [15] in the literature, where citral was successfully transformed to menthols. In citral transformation maximally 89% menthols were formed over 3 wt.% Ni-H-MCM-41 catalyst under 70 °C and 5 bar hydrogen in toluene after 300 min. The menthol mixture consisted of 70–75% menthols, 15–20% neomenthols and 5–10% isomenthols. Additionally 10% of by-products due to decarbonylation and cracking were formed in that work [15]. The metal selection, however was crucial for the production of menthols. When Pd/Beta was used as a catalyst in menthol synthesis, the major product was 3,7-dimethyloctanal [15]. Citral, which is a renewable raw material obtained via distillation of essential oils could be, however, a more attractive raw material than citronellal. In our previous attempt to transform citral directly to menthols

[16] over Ni-H-Y catalyst the main products were formed via cracking, dehydrogenation and cyclisation. The conclusion in that work was that the large amounts of Brønsted acid sites promoted the undesirable side reactions. Since later Trasarti et al. [15] were able to produce successfully menthols from citral, we wanted to reinvestigate Ni-H-Y and compare its performance directly with Ni-H-MCM-41, which contains less Brønsted acid sites. Moreover the effect of metal was of interest. The main aim was to demonstrate, how feasible Ni-H-MCM-41 is as a catalyst for producing menthols in one-pot from citral. Another aim was to elucidate the reaction mechanism, more precisely hydrogenolysis reactions, which should be suppressed in citral transformation. In order to be able to elucidate the reaction mechanism the more advanced tools, like mass spectrometry and chemometry were applied in this work. Two different bifunctional Ni catalysts supported on H-MCM-41 and H-Y were used in citral transformation in a hydrophobic solvent. It turned out that H-MCM-41 support was the most efficient one. Therefore the effect of metal was additionally investigated on this support.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

#### 2.1.1. Catalyst synthesis

Synthesis of the Na/MCM-41 mesoporous molecular sieve was carried out in 300 ml autoclave using a method described in Refs. [17,18]. As raw materials for Na/MCM-41 following chemicals were used: fumed silica (Aldrich), tetramethylammonium silicate (TMSiO<sub>2</sub>, Sachem), sodium silicate (Na<sub>4</sub>O<sub>4</sub>Si, Merck), tetradecyl trimethyl ammonium bromide (CH<sub>3</sub>(CH<sub>2</sub>)<sub>13</sub>N(CH<sub>3</sub>)<sub>3</sub>Br, Aldrich) and aluminium isopropoxide ((CH<sub>3</sub>)<sub>2</sub>CHO)<sub>3</sub>Al, Aldrich) as aluminium source. The Si/Al ratio was 20 for Na-H-MCM-41. The synthesis was carried out at 100 °C. After filtering the synthesized mesoporous material Na/MCM-41 was dried at 110 °C and ion-exchanged with 1 M NH<sub>4</sub>Cl for 24 followed by calcination at 530 °C. After drying at 110 °C the catalysts were calcined at 400 °C for 2 h. NH<sub>4</sub>-Y zeolite was supplied by Zeolyst International and H-Y was obtained by calcination of NH<sub>4</sub>-Y.

Metal modified catalysts were prepared by impregnating the support with a metal solution in a rotary evaporator for 24 h. As metal sources the following metal salts were used: ruthenium(III) chloride, (RuCl<sub>3</sub>·3H<sub>2</sub>O, Riedel-Haën), nickel(II) nitrate hexahydrate, (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Merck), palladium(II) nitrate dihydrate (Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, Fluka) and iridium chloride (IrCl<sub>4</sub>, Alfa Aesar). The nominal metal loading was 5 wt.% in all catalysts.

#### 2.1.2. Support and catalyst characterization

The specific surface areas of the catalysts were determined by nitrogen adsorption (Sorptometer 1900, Carlo Erba Instruments). The Dubinin method was applied for

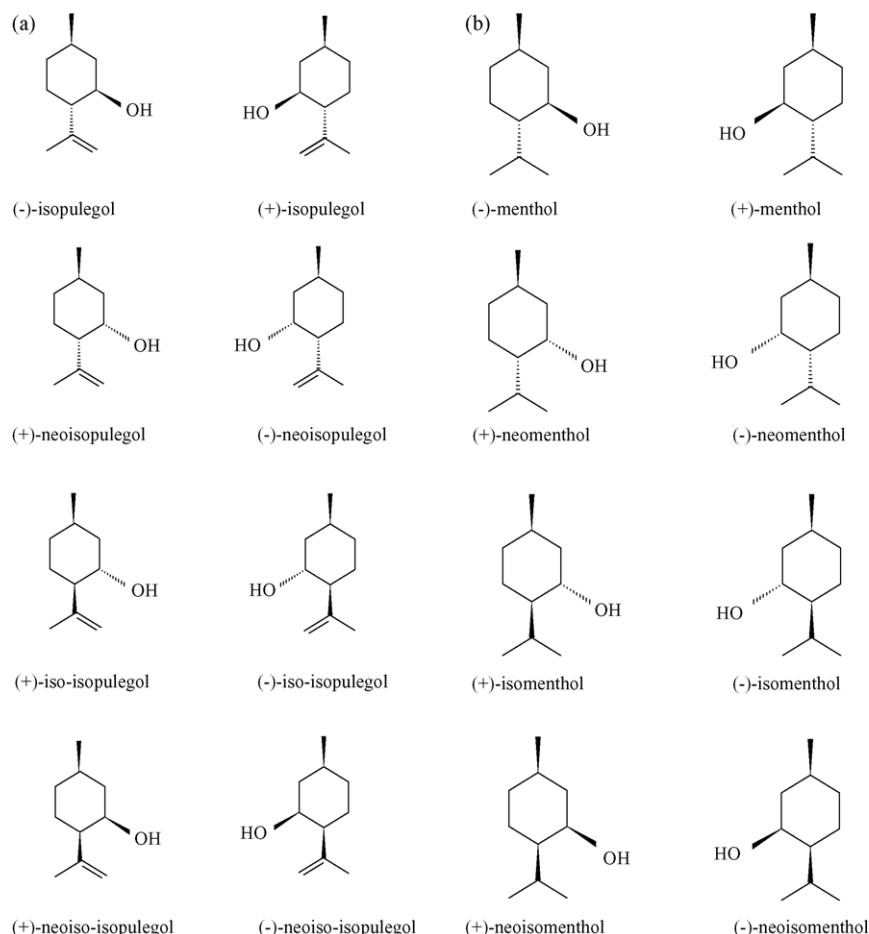


Fig. 2. The possible products from citral transformation to menthols (a) pulegols and (b) menthols.

calculating the surface area of H-Y, whereas BET method was used for H-MCM-41. The structure, phase purity and metal crystallite sizes of the reduced catalysts were determined by XRD (Philips PW1820 diffractometer) by using Cu K $\alpha$  radiation. The same catalyst reduction temperatures as reported in Section 2.2 were used in determination of metal crystallite sizes. The Cu-X-ray tube voltage was 40 kV and the current 50 mA. The samples were screened through an angular range of 0.5–90° ( $2\theta$ ) using 0.02° steps and 1 s measuring time for each step.

The quantitative measurements of the concentrations of Brønsted and Lewis acid sites in support materials were carried out by pyridine adsorption using infrared spectroscopy (ATI Mattson FT-IR). Thin wafers (10–12 mg/cm<sup>2</sup>) were prepared from support materials. The pyridine (>99.5%, a.r.) was adsorbed at 100 °C for 30 min and desorbed at 200 °C. The spectra was recorded at 100 °C with a spectral resolution of 2 cm<sup>-1</sup>. The molar extinction coefficient for pyridine determined by Emeis [19] was used for quantification.

## 2.2. Catalytic tests and analytics

Citral (97%, Lancaster 5460) was hydrogenated in a pressurized reactor (Autoclave Engineers, 500 ml) under

10 bar hydrogen (AGA, 99.999%) at 70 °C in cyclohexane. The catalysts were reduced in situ at 400 °C for 60 min with flowing hydrogen, except for Ru-H-MCM-41 (200 °C for 2 h) and Pd-H-MCM-41 (100 °C, 1 h). After cooling the catalyst to the reaction temperature the deoxygenated solvent including citral was injected in to the reactor. The reaction was started when the desired temperature and pressure were reached. The stirring rate was 1500 rpm. The hydrogenation was carried out under kinetic regime [20] with the catalyst particles below 90  $\mu$ m. The initial citral concentration was 0.01 M and the total liquid phase volume was 200 ml. Typically 300 mg catalyst was used in the hydrogenation experiments. Additionally citral transformations were investigated with a support material, i.e. H-MCM-41, under nitrogen (AGA) atmosphere at 70 °C and 10 bar. The samples were taken from the reactor and analyzed by a gas chromatograph equipped with a capillary column DB-1 (length 30 m, internal diameter 0.25 mm, film thickness 0.50  $\mu$ m). The detector and injector temperatures were 280 and 250 °C, respectively. The temperature programme used for separating the compounds was the following: 110 °C (1 min), 0.40 °C/min; 130 °C, 15 °C/min; 160 °C. The split ratio was 40:1. The peaks in the chromatogram were identified with following reference substances: citronellal

(93%, Acros), (–)-Isopulegol (99.5%, Fluka 59770), menthol (99%, Aldrich, M277–2), (+)-neomenthol (>99%, Chemica 72134), (–)-isomenthol (>99%, Chemica 58929), citronellal (98%, Fluka 27468), citronellol (90–95%, Fluka 27486), 3,7-dimethyloctanol (Aldrich 30577–4), geraniol (techn. %, Lancaster 6238) and nerol (90%, Fluka 72170) and with GC–MS. Different isopulegols synthesized in laboratory were identified by NMR [4]. Several peaks in the region of elution of the hydrogenolysis products consisted of co-eluting compounds. Software package Xtricator 2.0 [21] was used to resolve their chromatographic and spectral profiles in all overlapped peaks. The concentration and identity of individual compounds were determined from the resolved chromatographic and spectral profiles, respectively.

### 3. Results and discussion

#### 3.1. Support and catalyst characterization

The specific surface areas of different support materials decreased in the following order: H-Y > H-MCM-41 (Table 1). The specific surface area of the reduced 5 wt.% Ni-H-MCM-41 catalyst was 1051 m<sup>2</sup>/g<sub>cat.</sub>, which was larger than the specific surface area of MCM-41. This phenomenon can be explained by the heat treatment of the catalyst, which opens the micropores in the mesoporous material. The specific surface area of the spent Ni-H-MCM-41 catalyst was additionally measured. After 386 min reaction time the specific surface area of Ni-H-MCM-41 was 896/m<sup>2</sup> g<sub>cat.</sub> indicating minor catalyst deactivation (see Section 3.2.1.2).

The acid site concentrations of different support materials measured by pyridine adsorption showed that H-MCM-41 exhibited, as expected, lower Brønsted acidity, whereas the concentration of Brønsted acid sites of H-Y was over three-fold higher than MCM-41.

The XRD measurements on Na-MCM-41 confirmed that the synthesized material exhibited similar XRD patterns as

Table 1

The specific surface area and the concentrations of Brønsted and Lewis acid sites of different supports

Support	The specific surface area (m <sup>2</sup> /g <sub>cat.</sub> )	Brønsted acid sites (μmol/g <sub>cat.</sub> )	Lewis acid sites (μmol/g <sub>cat.</sub> )
H-MCM-41	902	89	168
H-Y	1218	291	165

Table 2

The mean metal crystallite sizes in the catalysts

Catalyst	Metal crystallite size (nm)
Ni-H-MCM-41	5.8 [24]
Ni-H-Y	n.m.
Pd-H-MCM-41	7.1
Ru-H-MCM-41	<sup>a</sup>
Ir-H-MCM-41	11

<sup>a</sup> Below detection limit [22].

reported in the literature [22]. The crystallite sizes of the metal supported catalysts are shown in Table 2. Very highly dispersed Ru particles were present on H-MCM-41, since no Ru peak was recorded [23]. The metallic Ni (Fig. 3b), Pd and Ir phases were identified in the reduced catalysts supported on H-MCM-41 by XRD. Additionally the original structure of H-MCM-41 was intact after metal deposition (Fig. 3a). The sizes of Pd, Ir and Ni particles were relatively small (Table 2). The Ni particle size on H-Y was not measured.

#### 3.2. Catalytic results

##### 3.2.1. Effect of support

###### 3.2.1.1. Initial reaction rates over different Ni catalysts.

The initial total reaction rates for citral was higher over Ni-H-MCM-41 than over Ni-H-Y, while on the other hand the initial hydrogenolysis rate showed as the opposite behavior. A higher hydrogenolysis activity over Ni-H-Y correlated well with a higher concentration of Brønsted acid sites in this catalyst compared to Ni-H-MCM-41 (Table 1). The concentration of Lewis acid sites was nearly the same for both the supports and is not correlating with the catalytic data (see Tables 1 and 3). Additionally to the total initial rate the initial

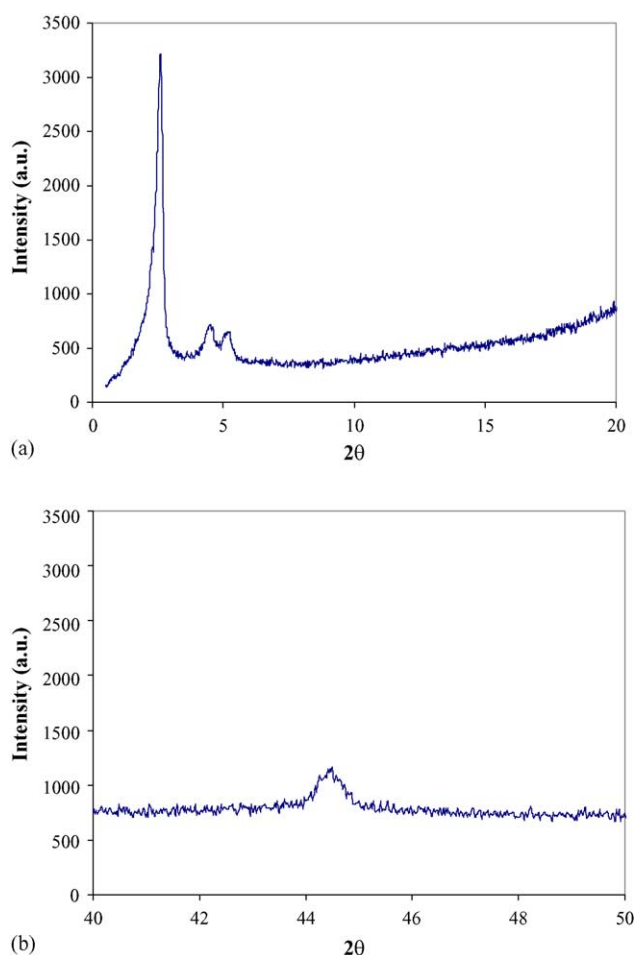


Fig. 3. XRD pattern for Ni-H-MCM-41.

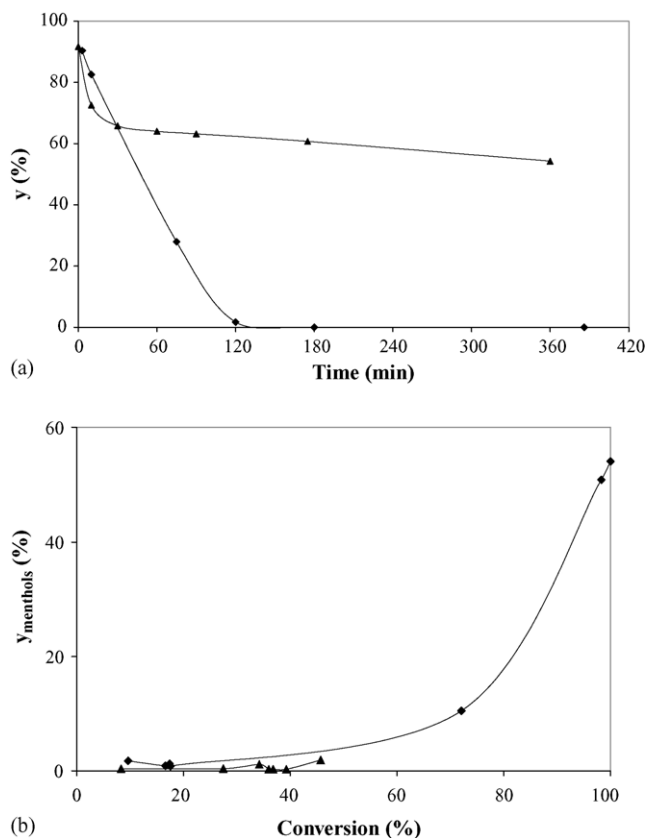


Fig. 4. (a) Kinetics for one-pot citral transformation and (b) yields of four menthols as a function of citral conversion over (◆) Ni-H-MCM-41 and (▲) Ni-H-Y.

hydrogenation rate was 5.2-fold lower over Ni-H-Y than over Ni-H-MCM-41. These results indicated that citral is very strongly adsorbed on the acidic sites on the catalyst support reacting further to hydrogenolysis products over Ni-H-Y.

**3.2.1.2. Conversion after prolonged reaction times over different Ni catalysts.** The complete conversion of citral occurred over Ni-H-MCM-41, whereas over Ni-H-Y the catalyst deactivated very fast (Table 3, Fig. 4a). The catalyst deactivation in Ni-H-MCM-41 was minor, which could be confirmed by comparing the specific surface area of the fresh and the spent Ni-H-MCM-41 catalyst after 390 min reaction time. The specific surface area of Ni-H-MCM-41 decreased only 15% from its original value (see Section 3.1). Previously it has been reported [24] that the structure of Ni-H-MCM-41 remained intact during catalytic isomerization of linoleic acid. The decrease of the specific surface area of Ni-H-MCM-41 suggests that the reason for catalyst deactivation is thus pore blockage during citral transformation due to accumulation of organic material in the micropores of MCM-41. The citral conversion over Ni-H-Y after 330 min was 45%. Over this catalyst the total reaction rate decreased from the initial total rate of 0.19–0.004 mmol/min g<sub>cat.</sub> after 30 min reaction time (Fig. 4a). This rate decrease can be correlated to the fast catalyst deactivation caused by the formation

Table 3  
Initial total reaction rate<sup>a</sup>, initial hydrogenation rate<sup>b</sup>, initial hydrogenolysis rate<sup>c</sup> and selectivities to (±)-isopulegol, (±)-menthol and menthols in citral transformation over different Ni catalysts supported on zeolites and mesoporous materials in cyclohexane under 10 bar hydrogen and at 70 °C

Catalyst	Total reaction rate (mmol/min g <sub>cat.</sub> )	Initial hydrogenation rate (mmol/min g <sub>Ni</sub> )	Initial hydrogenolysis rate (mmol/min g <sub>cat.</sub> )	Conversion after 330 min	Selectivity to (±)-isopulegol <sup>c</sup> (%)	Selectivity to (±)-menthol (%)	Selectivity to menthols after 330 min (%)	Yield of hydrogenolysis products after 330 min (%)
Ni-H-MCM-41	0.25	4.2	0.04	100	2	10 <sup>d</sup>	54	40
Ni-H-Y	0.19	0.8	0.15	42	<1	<1 <sup>c</sup>	4	35

<sup>a</sup> Calculated per gram catalyst.

<sup>b</sup> Calculated per gram Ni.

<sup>c</sup> At 20% conversion level.

<sup>d</sup> At 80% conversion level.



of hydrogenolysis products. The yield of hydrogenolysis products over Ni-H-Y after 10 min reaction time was 25%. Very fast catalyst deactivation is connected to the high concentration of acid sites in Ni-H-Y. Over Ni-H-MCM-41 the initial conversion of *cis* citral was quite fast within first 15 min reaction time after which both *cis* and *trans* citral converted with the same rates, i.e. the ratio *cis* to *trans* citral decreased from 0.33 to the value 0.23 within 15 min after which it was constant. The yield of pulegols formed over Ni-H-MCM-41 remained below 3% within first 15 min reaction time. The concentration of Brønsted acid sites is a decisive factor for achieving high conversions of citral. Over the catalyst containing the highest concentration of Brønsted acid sites, namely over Ni-H-Y the citral conversion remained relatively low due to extensive catalyst deactivation.

**3.2.1.3. Selectivity in citral transformation over different Ni catalysts.** The most selective catalyst for menthols was Ni-H-MCM-41 (Fig. 4a, Table 3). The maximum yield of four menthols at 100% conversion of citral over Ni-H-MCM-41 was 54%. The stereoselective ratio of ( $\pm$ )-menthols:( $\pm$ )-neomenthols:( $\pm$ )-isomenthols was 71%:25%:4%. No ( $\pm$ )-neoisomenthols were detected in the reaction mixture. This ratio is comparative to the data of Trasarti et al. [15]. The stereodirective step in menthol formation is occurring in the cyclisation of citronellal, as shown in our previous paper [4]. The amount of hydrogenolysis products over Ni-H-MCM-41 at 100% conversion was about 43% (Table 3, Fig. 4c). The most acidic catalyst, i.e. Ni-H-Y was not selective for menthol formation. The maximum yields of menthols over this catalyst were below 2%. Over Ni-H-Y catalyst the main products came from hydrogenolysis, about 38 at 48% conversion after 360 min. This result is in accordance with our previous result from citral hydrogenation in 2-pentanol over Ni-H-Y, which yielded mostly hydrogenolysis, dehydrogenation, cracking and acetalization products [16]. The main side products in citral transformation over different catalysts were analyzed by GC–MS and they are discussed in Section 3.2.3.

It can be concluded that Ni-H-Y catalyst is too acidic for citral hydrogenation, whereas the most suitable support for menthol synthesis starting from citral was H-MCM-41. Based on the comparison of H-Y and H-MCM-41 supports in menthol synthesis the effect of metal in citral hydrogenation to menthols was studied on mesoporous H-MCM-41 and is reported below. It should be noted, that the reported data does not allow, however, speculation of the origin of the selective performance of MCM-41 support and further research is needed to answer the question if either the special pore structure or/and mild acidity, etc, are responsible for high selectivity.

### 3.2.2. Effect of metal

**3.2.2.1. Initial reaction rates.** Four different metals supported on H-MCM-41 were investigated in citral hydrogenation. The initial total reaction rates decreased in the following order: Pd-H-MCM-41 > Ir-H-MCM-41 > Ni-H-

Table 4  
Initial total reaction rate<sup>a</sup>, initial hydrogenation rate<sup>b</sup>, initial hydrogenolysis rate<sup>a</sup>, conversion of citral and selectivities to ( $\pm$ )-isopulegol, ( $\pm$ )-menthol in citral transformation over different metals supported on H-MCM-41 in cyclohexane under 10 bar hydrogen and 70 °C

Catalyst	Total reaction rate (mmol/min g <sub>cat.</sub> )	Initial hydrogenation rate (mmol/min g <sub>metal</sub> )	Initial hydrogenolysis rate (mmol/min g <sub>cat.</sub> )	Conversion after 330 min (%)	Selectivity to ( $\pm$ )-isopulegol <sup>c</sup> (%)	Selectivity to ( $\pm$ )-menthol <sup>d</sup> (%)	Selectivity to menthols after 330 min (%)	Yield of hydrogenolysis products after 330 min (%)
Ni-H-MCM-41	0.25	4.2	0.04	100	14	10	54	40
Pd-H-MCM-41	1.87	36.6	0.04	100	8	13	44	18
Ru-H-MCM-41	0.13	1.6	0.05	95	13	1	4	27
Ir-H-MCM-41	0.9	1.3	0.88	86	1	<1	<1	82

<sup>a</sup> Calculated per gram catalyst.

<sup>b</sup> Calculated per gram metal.

<sup>c</sup> 50% conversion.

<sup>d</sup> 80% conversion.

MCM-41 > Ru-H-MCM-41 (Table 4). When hydrogenation and hydrogenolysis rates were separated, it turned out that the highest initial hydrogenation rate was observed for Pd followed by Ni, Ru and Ir. The hydrogenolysis was very prominent on Ir, whereas all other metals exhibited very low initial hydrogenolysis activity.

**3.2.2.2. Conversion after prolonged reaction times.** Conversion after 330 min was 100% over Pd-H-MCM-41 and Ni-H-MCM-41 catalysts, whereas over Ru and Ir slightly lower conversion levels were achieved, i.e. 95 and 86%, respectively (Table 4). The most active hydrogenation catalyst initially was Pd-H-MCM-41, over which 57% citral had converted within 2 min and citral reacted to completion (Fig. 5a). A minor catalyst deactivation occurred in Ni-H-MCM-41 after 5 min reaction time, thereafter the reaction proceeded with five times lower rate (0.02 mmol/min  $g_{cat.}$ ) than the initial total reaction rate. Over Ru-H-MCM-41 catalyst deactivation became visible after 30 min reaction time, thereafter citral converted with a decreased reaction rate (Fig. 5a). The total initial reaction rate and total reaction rate in 30 min over Ru-H-MCM-41 catalyst were 0.13 mmol/min  $g_{cat.}$  (Table 4) and 0.008 mmol/min  $g_{cat.}$ , respectively. The Ru surface kept, however, its activity for hydrogenation, because the reaction rate remained constant until 332 min reaction time. Over Ir-H-MCM-41 catalyst the catalytic activity decreased very much after 2 min from the initial total reaction rate

of 0.9 to 0.02 mmol/min  $g_{cat.}$ . After 15 min reaction time already 40% hydrogenolysis products were formed and the total yield of hydrogenation and cyclisation products was below 3%. Finally the catalytic activity was close to zero after 120 min reaction time and the yield of hydrogenolysis products was 82% after 348 min. The reason for the extensive catalyst deactivation over Ir-H-MCM-41 was very prominent hydrogenolysis, which forms coke on the metal surface.

**3.2.2.3. Selectivity.** The selectivities to ( $\pm$ )-isopulegols and ( $\pm$ )-menthols are given in Table 4 at certain conversion levels. Additionally the total selectivity to four menthols and the yields of hydrogenolysis products after 330 min are given in Table 4. The yields of menthols versus citral conversion are shown in Fig. 5b from which it can be seen that menthol formation is more prominent at higher citral conversion levels. In order to clarify, whether the citral transformation to menthols is a consecutive reaction, the yields of pulegols are plotted against yields of menthols (Fig. 5c). The kinetic analysis of the yields of pulegols and menthols exhibited a typical pattern of a consecutive reaction suggesting that the one-pot synthesis of menthols from citral is feasible. The challenge is, however, to suppress the parallel hydrogenolysis reaction of citral. The formation of hydrogenolysis products as a function of citral conversion over different metal supported MCM-41 catalysts is shown in Fig. 5d.

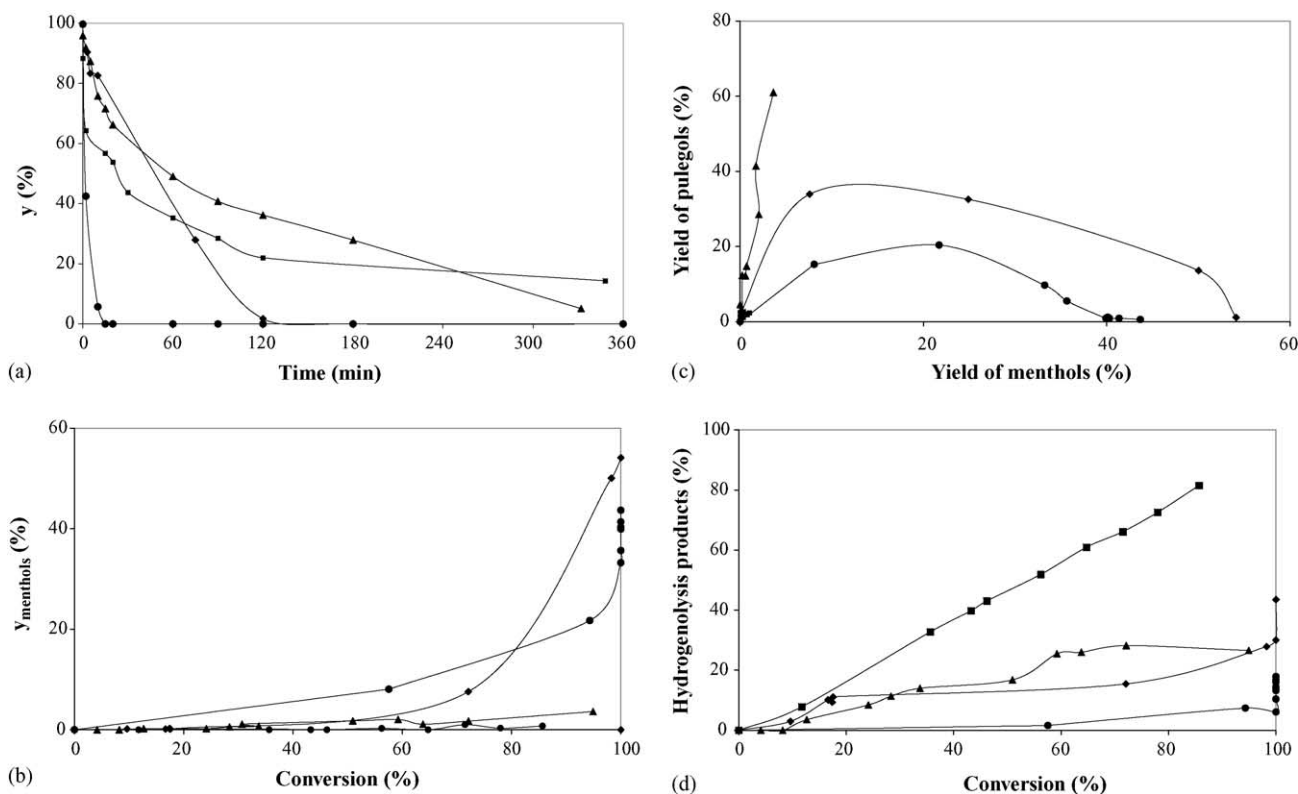


Fig. 5. (a) Kinetics for one-pot citral transformation, (b) yields of four stereoisomers of menthols, (c) the yields of pulegols versus the yields of menthols and (d) yields of hydrogenolysis products over (◆) Ni-H-MCM-41, (●) Pd-H-MCM-41, (▲) Ru-H-MCM-41 and (■) Ir-H-MCM-41.

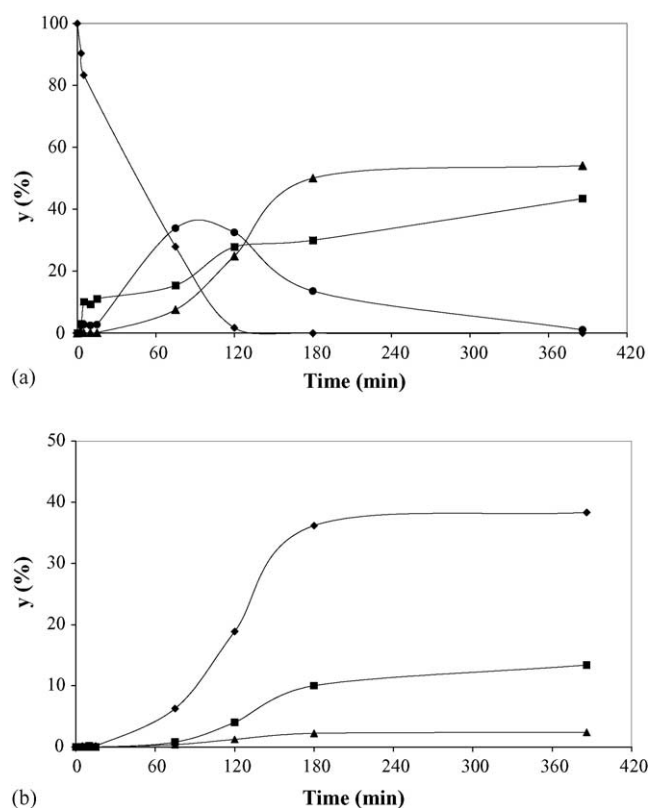


Fig. 6. (a) Kinetics for one-pot citral transformation, symbols (◆) citral, (●) pulegols, (▲) menthols and (■) hydrogenolysis products; (b) yields of (◆) (±)-menthols, (■) (±)-neomenthols and (▲) (±)-isomenthols over Ni-H-MCM-41. No (±)-neoisomenthols were formed.

The effect of metal on the citral transformation to menthols over an acidic support is clearly visible from Fig. 5b. The most selective catalyst for producing menthols was Pd-H-MCM-41 at conversion levels below 80% (Fig. 5b). Maximally 20% stereoisomers of four pulegols were formed over Pd-H-MCM-41 catalyst at citral conversion of 94%. The hydrogenation rate of pulegols to menthols was maximally 1.4 mmol/min  $g_{\text{metal}}$ . The selectivity over the Pd-H-MCM-41 catalyst at higher conversion levels was decreased by the formation of 3,7-dimethyloctanal and 3,7-dimethyloctanol. After 360 min the yields of these products were 21 and 16%, respectively. Therefore at higher conversion level, between 80 and 100% Ni-H-MCM-41 was the most selective catalyst. The formation of three major menthols is shown in Fig. 6b. Maximum amount of four pulegols, about 33%, over Ni-H-MCM-41 were formed at 72% conversion of citral at the reaction time of 75 min (Fig. 6a). The hydrogenation rate of pulegols after this point was 0.30 mmol/min  $g_{\text{metal}}$ . Comparing the hydrogenation activity of pulegols over Pd-H-MCM-41 and Ni-H-MCM-41 it can be stated that the former catalyst was 4.7 times more active in the hydrogenation of pulegols to menthols than Ni-H-MCM-41. In general Pd is known to be very active in the hydrogenation of ethylenic double bonds.

Opposite to Ni and Pd, Ru and Ir supported on H-MCM-41 were not selective to menthols (Table 4, Fig. 5b). The maximum selectivities to menthols over Ru-H-MCM-41 and over Ir-H-MCM-41 catalysts were only 4% after 332 min and <1% after 348 min, respectively. The reasons for low menthol selectivities were, however, different over Ru- and over Ir-H-MCM-41 catalysts. The low selectivity to menthols over the former catalyst was caused by the fact, that the hydrogenation rate for pulegols was very slow over this catalyst. The total yield of four pulegols was 61% after 330 min. Opposite to Ru-H-MCM-41 the low selectivity to four menthols over Ir-H-MCM-41 is explained by the extensive hydrogenolysis reaction (Fig. 5d). The total yield of hydrogenolysis products over Ir-H-MCM-41 after 348 min was 82%. It has been reported that Ir/Beta catalyst was selective to menthols in citronellal transformation [14], but in citral hydrogenation Ir-H-MCM-41 was not a suitable catalyst. Over Ir-H-MCM-41 *cis* citral converted very fast to the hydrogenolysis products followed by the hydrogenolysis reaction of *trans* citral. Maximally only 2% pulegols were formed from citral over Ir-H-MCM-41 catalyst.

The effect of metal on the hydrogenolysis activity during citral transformation is in accordance with literature [25,26]. In thymol hydrogenation [25] Ir favored formation of hydrocarbons originated from menthone and isomenthone. Furthermore Ru is more active in the hydrogenolysis of allylic compounds than Pd [26]. It can be concluded that both the selection of support and metal have a large effect on the hydrogenolysis of citral.

### 3.2.3. Formation of by-products from citral transformation over bifunctional metal supported catalysts

The bifunctional catalysts catalyzed both hydrogenation and cyclisation as well as hydrogenolysis, isomerisation and dehydration. Over the most selective catalyst, i.e. over Ni-H-MCM-41 totally 40% hydrogenolysis products were formed after 330 min (Table 3). The main hydrogenolysis products confirmed by GC-MS in the beginning of the experiment were menthatrienes (three different isomers as major products), aromatic compounds exhibiting the molecular mass of 134 and menthadienes. At 24% conversion of citral the relative amounts of menthatrienes, aromatics and menthadienes were 26, 18 and 48%, respectively. After 386 min reaction time the main hydrogenolysis products were monoenes and dienes, 66 and 25%, respectively, whereas only 1% aromatic compounds were present within the hydrogenolysis products. The menthatrienes, which were confirmed by GC-MS were 1,3,8(9)-menthatriene, 1(7)2,8(9)-menthatriene. 1,4(5),8(9)-menthatriene may be present also. These products are formed via acid catalyzed dehydration from citral followed by acid catalyzed rearrangements of double bonds. The following dienes were confirmed among the reaction products:  $\alpha$ -phellandrene, limonene and  $\alpha$ -terpinene. Dienes are further hydrogenated to monoenes, like 4-methyl-(1-methylethyl)cyclohexene and 1-methyl-4-(1-methylethyl)cyclohexene. The



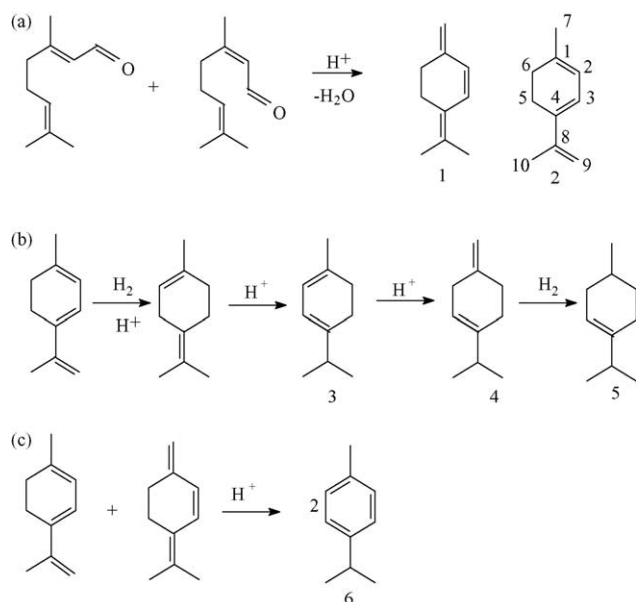


Fig. 7. Examples of possible side reactions in citral transformation over bifunctional catalysts, (a) citral transformation to menthatrienes, 1(7),2,4(8)-menthatriene (1) and 1,3,8(9)-menthatriene (2); (b) menthatriene hydrogenation and acid catalyzed rearrangement to dienes,  $\alpha$ -phellandrene (3),  $\alpha$ -terpinene (4) and 1-methyl-4-(1-methylethyl)cyclohexene (5); (c) acid catalyzed arrangement of citral to  $p$ -cymene (6).

aromatic part contained  $p$ -cymene, which can be formed from menthatriene via acid catalyzed rearrangement (Fig. 7c). In the hydrogenation of menthatrienes, menthadienes (Fig. 7b) and menthenes were formed. Additionally it was confirmed that no metal and hydrogen are needed in the formation of menthatrienes from citral. When citral was contacted with H-MCM-41 at 70 °C in cyclohexane as a solvent under air, the GC–MS analysis showed the presence of three menthatrienes. The two major menthatrienes (1 and 2 in Fig. 7a) gave a base peak at  $m/e = 91$  by loss of a molecular fragment with  $m/e = 43$  from the molecular mass of 134. This fragment corresponds to an isopropyl group. Menthane and its mono-, di- and triene derivatives easily lose such a fragment even when the substituent at C-4 is isopropylidene as in 1 or isopropenyl as in 2 (Fig. 7a) [28]. The proportions of menthatrienes were initially 29:51:19.

Citral is hydrogenolyzed over heterogeneous catalysts containing Brønsted acid sites. The extent of citral hydrogenolysis over Ni-H-MCM-41 in this work was more prominent than reported by Trasarti et al. [15]. In their work about 11% of other products were obtained at the same reaction temperature, whereas hydrogen pressure was 5 bar compared to 10 bar in the current work. Additionally Trasarti et al. [15] used toluene, while cyclohexane was applied in this work. When comparing the catalysts in [15] and in the present study, it can be stated that the ratio between Lewis and Brønsted acid sites is 2.5 and 1.8, respectively, indicating that the latter catalyst would contain less Brønsted acid sites. Thus the different amounts of hydrogenolysis products,

e.g. the higher extent of hydrogenolysis in the current work cannot be explained only based on acidities.

Over more acidic Ni-H-Y catalyst the dehydrogenation occurred after 330 min reaction time leading to the formation of 22 and 16% of  $p$ -cymene, respectively. This catalyst exhibited the highest concentration of Brønsted acid sites and the product mixture over the former catalyst after 360 min contained 18% of aromatic compounds, 8% of menthatrienes, 6% of menthadienes and only 0.5% of menthenes.  $p$ -Cymene was formed also in acid catalyzed dehydration of citral with 20 wt.% sulphuric acid [27] confirming thus the importance of Brønsted acid sites in citral dehydration. On the other hand, dehydrogenation of hydrocarbons is possible without hydrogen over metal surfaces already at very low temperatures. In a separate experiment, where citral was reacting in cyclohexane at 70 °C and under 10 bar of hydrogen over H-MCM-41, the corresponding citral conversion was 39% after 60 min. The molar *cis/trans* ratio in citral declined linearly from 0.5 to nearly zero with the slope of 1.4 with increasing citral conversion indicating that *cis* citral was more reactive *trans* citral over acid catalyst surfaces. The main products in these experiments were two isomers of menthatrienes.

The metal selection had a large effect on the hydrogenolysis reaction. Over Ir-H-MCM-41 totally 82% hydrogenolysis products were formed (Table 4). At citral conversion of 60% the total amount of hydrogenolysis products was 34%. The major compounds in hydrogenolysis products were menthatrienes (13%), menthadienes (7%) and  $p$ -cymene (4%). Hydrogenolysis of citral proceeded from menthatrienes further to menthadienes and menthenes. However, opposite to Ni-H-MCM-41 the citral hydrogenolysis proceeds further to hydrogenated products 1-methyl-4-(1-methylethyl)cyclohexanes and to dehydrogenated  $p$ -cymene over Ir-H-MCM-41. These compounds were confirmed by GC–MS in the reaction mixture after 348 min.

#### 4. Conclusions

Ni catalysts supported on zeolite and mesoporous support materials were investigated in citral hydrogenation for the synthesis of ( $\pm$ )-menthols. Additionally, the effect of the metal was studied on H-MCM-41 mesoporous molecular sieve.

There was a clear support effect on the initial reaction rate. The initial total reaction rate of citral was the highest one over Ni-H-MCM-41 followed by Ni-H-Y. The catalyst deactivation was the very prominent over Ni-H-Y, which exhibited the highest concentration of Brønsted acid sites.

For different metals supported on MCM-41 it can be concluded that the most active catalyst was Pd-H-MCM-41 followed by Ni-H-MCM-41, Ir-H-MCM-41 and Ru-H-MCM-41. The catalyst deactivation was very low over Ni-H-MCM-41 catalyst, whereas it was very prominent over Ir-H-MCM-41 and Ru-H-MCM-41 catalysts. Over the same H-MCM-41 support the hydrogenolysis activity decreased

in the following order: Ir  $\gg$  Ni > Ru > Pd. The catalyst deactivation originated from coking, i.e. the accumulation of organic material inside the catalyst, since the structure of H-MCM-41 remained intact.

The most selective catalyst for the formation of menthols at conversions below 80% was Pd-H-MCM-41, whereas at higher conversion levels Ni-H-MCM-41 was the most promising catalyst. This work demonstrated the feasibility of one-pot synthesis of menthol from citral, since the kinetic data exhibited the typical consecutive reaction mechanism from pulegols to menthols. The challenge is, however, to suppress the parallel hydrogenolysis reaction starting from citral. The crucial point in catalyst development for one-pot transformation of citral to menthols, is the metal and support selection. Further optimization is, however, needed for increasing selectivity to menthols by tuning the catalyst acidity, metal loading and reaction conditions.

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