One-step microwave-assisted asymmetric cyclisation/hydrogenation of citronellal to menthols using supported nanoparticles on mesoporous materials†

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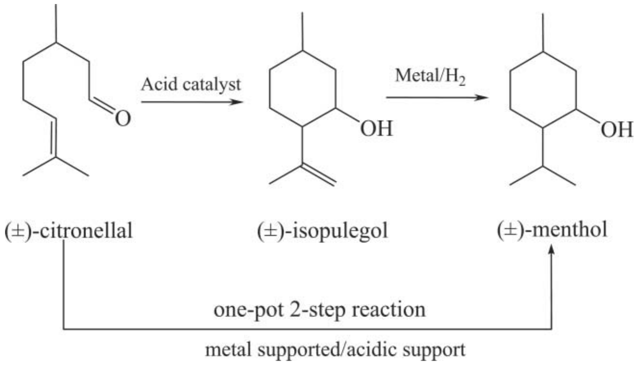
Received 26th February 2010, Accepted 7th April 2010
First published as an Advance Article on the web 29th April 2010
DOI: 10.1039/c003600e

The selective conversion of citronellal to menthols, with good diastereoselectivities to (–)-menthol for the case of (+)-citronellal as starting material, can effectively be carried out in a one-step reaction under microwave irradiation catalysed by supported nanoparticles on mesoporous materials. 2% Pt/Ga-MCM-41 was found to be the optimum catalyst for the reaction, with a quantitative conversion of starting material and selectivities above 85% to menthols obtained in short reaction times (typically 15 min). These results constitute the first report of a simple microwave-assisted one-step cyclisation/hydrogenation process for the production of menthols.

Introduction

Menthol is among the most demanded chemicals in industry, with a wide range of uses in pharmaceuticals, agrochemicals, cosmetics, flavourings and personal-care applications.[1] Despite the many industrial applications of racemic (±)-menthol, (–)-menthol is actually the compound that exhibits the characteristic peppermint odour and unique cooling sensation.[1] At an industrial scale, the Takasago process is one of the major routes currently utilised for menthol production. It involves the cyclisation and isomerisation of (+)-citronellal to (–)-isopulegol (Scheme 1, first step) using $ZnBr_2$ as catalyst,[1–3] followed by a hydrogenation of the *exo*-double bond in the isopulegol to give (–)-menthol (Scheme 1, second step).



Scheme 1 Production of menthols from (±)-citronellal using heterogeneous catalysts.

For the first step (citronellal cyclisation), the use of a wide variety of heterogeneous catalysts including Lewis acid supported catalysts,[2,4] heteropolyacids[5] and metal fluorides[1] has been reported to replace the very selective and active conventional homogeneous methodologies that were able to give isopulegol yields up to 99.3%.[6] For the second step (hydrogenation of the double bond in isopulegol), a conventional metal-reducing step under hydrogen has been reported to provide high selectivities to menthols (>93%, with diastereoselectivities of 85%).[7] However, despite several attempts to combine these reactions into a one-step process,[7,8] currently there is no simple, mild, and environmentally friendly methodology that can provide good yields of menthols in a one-step process, at short reaction times under mild conditions.

In our recent work in the area of supported nanoparticles on porous materials, we have demonstrated that a wide range of functionalities including ketones and aldehydes could be easily hydrogenated using a simple and efficient microwave-assisted transfer hydrogenation (TH) system with 2-propanol as a stable hydrogen donor.[9] In parallel to these studies, a significant variety of supported metal and metal oxide nanoparticles (SMNPs) including Au, Ag, Fe, Cu, Pt and Pd on a variety of porous materials have also been prepared and investigated in a number of heterogeneously catalysed processes.[10–12]

Herein, we report the use of versatile heterogeneous catalytic systems in the asymmetric chemical transformation of (±)-or (+)-citronellal to (±)-menthols, with high diastereoselectivities to (–)-menthol, *via* one-step cyclisation/hydrogenation promoted under microwave irradiation and mild reaction conditions.

Experimental

Ga- and Al-MCM-41 supports were prepared using previously reported protocols,[13] in a similar way to the Al- and/or Ga-SBA-15 employed as supports.[14] In this way, Ga- and Al-MCM-41 and SBA-15 materials with Si/Al 15 ratio were synthesized.

A typical methodology to prepare supported Pd, Pt and Cu materials was performed under microwave irradiation in a similar way to a previously reported protocol[9] as follows: 0.4 g pre-synthesized support and 15 mL of a water solution containing the needed quantity of metal salt precursor (tetraamine platinum(II) nitrate, palladium(II) acetate or copper(II) chloride) to achieve a

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† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c003600e

2% loading were added to a round-bottomed flask and microwaved for 30 min in a CEM-Discover microwave reactor in open-vessel mode. The final solid was then placed in a rotary evaporator for around 30 min, subsequently calcined at 550 °C for 4 h and further reduced under hydrogen stream for 2 h (50 mL min^{-1}) at 400 °C to ensure the generation of supported metal nanoparticles.

Materials characterisation

Materials were characterised by means of porosimetry, pyridine titration and elemental analysis. N_2 adsorption measurements were performed in a volumetric adsorption analyser Micromeritics ASAP 2000. Samples were degassed for 24 h at 100 °C under vacuum ($p < 10^{-2}$ Pa) and subsequently analysed.

Pyridine (PY) titration was carried out using a previously reported gas-chromatography methodology.[15]

Elemental analysis was performed using Inductively Coupled Plasma (ICP) in a Philips PU 70000 sequential spectrometer equipped with an Echelle monochromator (0.0075 nm resolution). Samples were digested in HNO_3 and subsequently analysed by ICP.

XPS measurements were performed in a ultra high vacuum (UHV) multipurpose surface analysis system (SpecsTM model, Germany) operating at pressures <10–10 mbar using a conventional X-ray source (XR-50, Specs, Mg–K, 1253.6 eV) in a "stop-and-go" mode to reduce potential damage due to sample irradiation. Survey and detailed Cu high-resolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature with a Phoibos 150-MCD energy analyser. Powdered samples were deposited on a sample holder using double-sided adhesive tape and subsequently evacuated under vacuum ($<10^{-6}$ Torr) overnight. Eventually, the sample holder containing the degassed sample was transferred to the analysis chamber for XPS studies. Binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon.

Catalytic activity

Microwave reaction experiments were carried out in a CEM-DISCOVER model with PC control and monitored by sampling aliquots of reaction mixture. Samples were analysed by GC/GC-MS using an Agilent 6890 N GC model fitted with a Rt-γDEXsa™ cyclodextrin based column (30 m, 0.25 i.d.) and an FID detector. Experiments were conducted in closed-vessel mode (10 mL, pressure controlled) under continuous stirring. The microwave method was generally power controlled where samples were irradiated at different power outputs and various temperatures were reached. The effect of the power, time of irradiation and quantity of catalyst in the reaction were investigated under optimised conditions.

In a typical experiment, 10 mmol citronellal (1.54 g), 5 mL 2-propanol, 1 mmol K_2CO_3 and 0.05 g catalyst were microwaved for 15 min at 100 W. The final mixture was then analysed by GC and GC-MS. Response factors of reaction products were determined with respect to the corresponding starting material from GC analysis using known compounds in calibration mixtures of specified compositions. Reaction products were also identified through their MS and ^1H NMR spectra (Bruker 300 MHz). Stereoselectivities were evaluated by GC with the chiral column that allows good separation of products as well as corroborated by ^1H NMR. Materials were also reused following the proposed methodology. With this purpose, 0.1 g catalyst (to facilitate the recovery of the catalyst in successive reuses) was utilised in the process under identical reaction conditions. Upon reaction completion, the catalyst was filtered off, washed thoroughly with acetone and ethanol, and oven-dried overnight at 120 °C prior to its reuse in the reaction.

Reaction runs with added chiral modifiers were performed as follows: the chiral modifier (few milligrams to reach a substrate/modifier 200/1 ratio) was dissolved in 2-propanol (1–2 mL) under gentle heating (30–50 °C), prior to its addition to a microwave tube. Then, the resulting solution was added to the typical reaction mixture (10 mmol citronellal, 3–4 mL 2-propanol, 1 mmol K_2CO_3 and 0.05 g catalyst) and eventually microwaved for 15 min at 100 W.

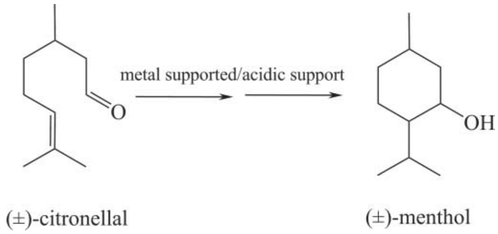
Results and discussion

Results for N_2 physisorption, PY titration and elemental analysis (metal content) experiments are summarised in Table 1. The metal content in the materials was close to the theoretical 2 wt% selected for the reaction, regardless of the metal (Pt, Pd or Cu) employed in their preparation (Table 1). XPS analysis of the materials showed Pd and Pt nanoparticles were mostly present as reduced metals (Pd^0 and Pt^0) on the supports while Cu nanoparticles were mostly present as reduced copper species (>60% total copper content, peaks at *ca.* 932–933 eV) and CuO (<40% of total copper content, characteristic shape-up peaks at 940–945 eV, only seen when Cu^{2+}

Table 1 Metal content (wt%, as measured by elemental analysis), textural properties and PY titration data (mmol PY adsorbed per gram of catalyst at 300 °C) of different supported metal nanoparticles on acidic mesoporous supports

Entry	Catalyst	Metal content (wt%)	Surface area/m^2 g^{-1}	Pore size/nm	Pore volume/mL g^{-1}	PY titration at 300 °C
1	Pd/Al-MCM-41	1.88	928	1.9	0.69	193
2	Pd/Ga-MCM-41	1.96	796	2.0	0.76	38
3	Pd/Al-SBA-15	1.96	903	5.9	0.81	185
4	Pd/Ga-SBA-15	1.92	799	4.5	0.83	65
5	Pt/Al-MCM-41	2.02	905	1.9	0.71	199
6	Pt/Ga-MCM-41	1.99	807	2.1	0.76	45
7	Pt/Al-SBA-15	1.87	910	6.0	0.82	181
8	Pt/Ga-SBA-15	1.89	812	4.6	0.89	70
9	Cu/Al-MCM-41	1.85	752	2.0	0.72	210
10	Cu/Ga-MCM-41	1.78	816	1.9	0.69	43
11	Cu/Al-SBA-15	1.98	890	6.0	0.85	230
12	Cu/Ga-SBA-15	1.93	824	4.6	0.87	68

Table 2 Catalytic performance [total conversion and selectivity to products ($S_{product}$, mol%) of supported nanoparticles on porous materials in the one-step microwave-assisted tandem cyclisation/hydrogenation of (±)-citronellal[a]



Entry	Catalyst	Conversion (mol%)	$S_{isopulegols}$ (mol%)	$S_{menthols}$ (mol%)	S_{others} (mol%)[c]
1	No catalyst[b]	<5	—	—	—
2	Al-MCM-41	78	70	Traces	30
3	Ga-MCM-41	59	>90	—	<10
4	Al-SBA-15	85	65	Traces	35
5	Ga-SBA-15	65	85	—	15
6	Pd/Al-MCM-41	>90	20	50	30
7	Pd/Ga-MCM-41	80	15	75	10
8	Pd/Al-SBA-15	>95	15	40	45
9	Pd/Ga-SBA-15	75	20	60	20
10	Pt/Al-MCM-41	95	15	60	25
11	Pt/Ga-MCM-41	>90	8	87	5
12	Pt/Al-SBA-15	>99	10	60	35
13	Pt/Ga-SBA-15	85	10	80	10
14	Cu/Al-MCM-41	90	30	30	40
15	Cu/Ga-MCM-41	75	50	40	10
16	Cu/Al-SBA-15	>95	25	30	45
17	Cu/Ga-SBA-15	85	35	50	15

[a] Reaction conditions: 10 mmol citronellal, 5 mL 2-propanol, 1 mmol K_2CO_3, 0.05 g catalyst, 100 W, 120–130 °C, 15 min reaction. [b] Blank run after 1 h microwave irradiation. [c] Other detected products include citronellol and byproducts from citronellal etherification and cracking.

Table 3 Effect of various parameters in the catalytic performance of 2% Pt–Ga-MCM-41 in the one-step microwave-assisted tandem cyclisation/hydrogenation of (±)-citronellal[a]

Reaction conditions	Conversion (mol%)	Selectivity to menthols (mol%)
Effect of the added quantity of catalyst		
100 W, 120–130 °C, **0.05 g cat.**, 15 min	>90	87
100 W, 120–130 °C, **0.1 g cat.**, 15 min	>99	75
100 W, 120–130 °C, **0.2 g cat.**, 15 min	>99	69
Effect of time of microwave irradiation		
100 W, 120–130 °C, 0.05 g cat., **10 min**	78	89
100 W, 120–130 °C, 0.05 g cat., **15 min**	>90	87
100 W, 120–130 °C, 0.05 g cat., **30 min**	>99	80
100 W, 120–130 °C, 0.05 g cat., **45 min**	>99	77
Effect of microwave power		
50 W, 100 °C, 0.05 g cat., 15 min	82	88
100 W, 125 °C, 0.05 g cat., 15 min	>90	87
150 W, 129 °C, 0.05 g cat., 15 min	>95	80
200 W, 130 °C, 0.05 g cat., 15 min	>99	70

[a] Reaction conditions: 10 mmol citronellal, 5 mL 2-propanol, 1 mmol K_2CO_3, 120–130 °C. Main reaction byproducts were citronellal etherification, cracking and dehydration compounds.

species are present), in good agreement with our previous reports both for Pd and/or Pt systems[9,11a,16] and Cu.[12a,12c]

Pyridine titration data showed different acidities between materials. These could be well correlated with the nature of the supports. Al-MCM-41 and Al-SBA-15 exhibited a remarkably higher total acidity compared to those of the analogous Ga-systems, while acidities of MCM-41 and SBA-15 materials were almost comparable (Table 1). Ga materials have been previously reported to have mostly Lewis acid sites[13a,14] while Al materials have a combination of both Lewis and Brønsted acid sites.[2,13b,15]

Materials were then tested for activity in the one-step cyclisation/hydrogenation of (±)-citronellal to (±)-menthols. Table 2 summarises the preliminary screening of catalysts and conditions in the proposed reaction. Acidity of the supports is believed to be sufficient to promote the cyclisation step, while the microwave conditions and the presence of supported nanoparticles could catalyse the hydrogenation of the double bond generated upon formation of isopulegol *via* hydrogen transfer (Scheme 1).

Blank runs (without catalyst) gave minimum conversion of starting material after 60 min microwave irradiation. Al and Ga materials provided relatively good conversions of starting material, with relatively high selectivities to isopulegols (Table 2, entries 2 to 5, superior to 80% for Ga materials) and minor selectivities to other products including citronellol (*via* isomerisation of citronellal on weak acid sites) as well as related byproducts from citronellal dehydration, cracking and/or etherification with 2-propanol employed as solvent/hydrogen donor in the reaction (Table 2, entries 3 and 5). These byproducts have been observed in catalysts containing higher and stronger acidities (*e.g.* Al-MCM-41 and Al-SBA-15).

2% Pt–Ga-MCM-41 was selected as an optimum material in terms of conversion and selectivity to menthols for the reaction, with its balanced combination of Lewis acidity of the support[13a,14] as well as superior hydrogenation activity of Pt compared to Cu and Pd nanoparticles. These findings were in good agreement with previous reports that claimed the cyclisation step is readily catalysed by strong Lewis and/or weak Brønsted acid sites[2,17] and it is actually the rate determining step in this process.[18]

The effect of different microwave parameters in the activity of the optimum 2% Pt–Ga-MCM-41 was subsequently investigated. The results in Table 3 gave an interesting insight into the effect of microwaves in the activity and selectivity of the systems. Microwaves have been reported to improve rates of reaction in many organic syntheses as well as sometimes selectivities to targeted products.[19]

An increase in the quantity of catalyst increased the conversions in the systems at the expense of menthol selectivity (Table 3, first three entries). Similar trends were found at increasing microwave power and times of reaction, although relatively high selectivities to menthols could still be obtained changing the latter (Table 3, middle entries).

The heterogeneous nature of the catalyst was then investigated under the reaction conditions. The results included in Fig. 1 demonstrated that 2% Pt–Ga-MCM-41 is a highly stable and reusable catalyst under the investigated microwave conditions, preserving over 90% of its initial activity after 3 reuses.

Interestingly, the selectivity to menthols was not significantly affected by the reuse of the catalyst. Nanoparticle sizes also remained unaltered upon reuse, with no aggregation of nanoparticles under the investigated reaction conditions. Pt nanoparticles were also found to be highly stable with no significant quantities of metal leached in solution (<2 ppm) after the reaction, as confirmed by

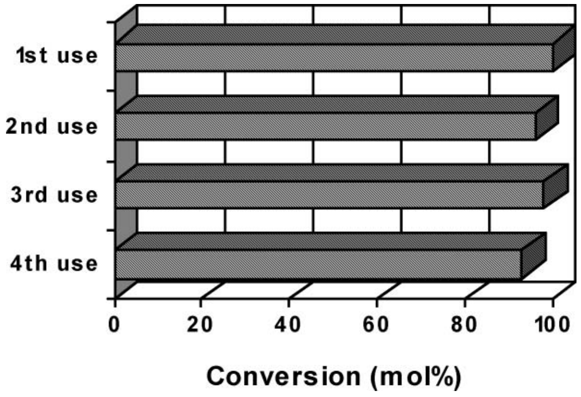
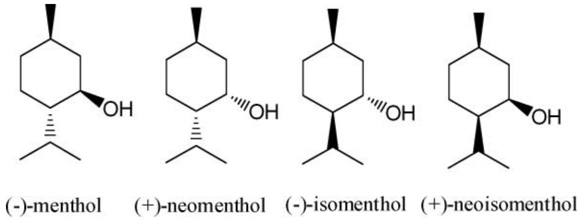


Fig. 1 Reuses of 2% Pt–Ga-MCM-41 catalyst in the one-step conversion of citronellal to menthols under microwave irradiation. Reaction conditions: 10 mmol citronellal, 5 mL 2-propanol, 1 mmol K_2CO_3, 0.1 g catalyst, 100 W, 120–130 °C, 15 min reaction.

ICP and the fact that no hydrogenation activity was observed in the final mixture filtrate (after 1 h of microwave irradiation) upon catalyst reuse.

Further studies were performed in order to investigate the diastereoselectivities in the optimised systems as well as the possibility to obtain (−)-menthol using (+)-citronellal and chiral catalysts/modifiers as alternatives. Stereoisomers that can be obtained in the reaction are included in Scheme 2 (for the particular case of enantiomerically pure citronellal), namely (−)-menthol, (+)-neomenthol, (−)-isomenthol and (+)-neoisomenthol.



Scheme 2 Stereoisomers obtained in the one-step tandem cyclisation/hydrogenation of (+)-citronellal.

The diastereoselectivity of the reaction was originally probed using racemic citronellal. Results included in Fig. 2 show two very interesting and different trends for the chosen catalytic systems (those providing the best activities/selectivities to menthols in Table 2).

For the Pd and Pt catalysts (showing the optimum selectivities to menthols), a maximum of 55% (±)-menthol was observed (2% Pt/Ga-MCM-41, out of the 87% selectivity to menthols), with varying quantities (5–20%) of other diastereisomers. Surprisingly, the poorly selective 2% Cu/Ga-SBA-15 material (only 50% menthol production) was found to have an outstanding 43% selectivity to (±)-menthol. Only minor quantities of (±)-neomenthol and (±)-isomenthol were observed in the reaction (Fig. 2).

We were also prompted to investigate whether higher diastereoselectivities to (−)-menthol could be obtained from enantiomerically pure (+)-citronellal. Studies showed the selectivities obtained for the investigated catalysts were slightly higher [*ca.* 60% (−)-menthol for the 2% Pt/Ga-MCM-41 material] but in any case very similar to those obtained from (±)-citronellal, implying the purity and diastereoselectivity of the starting material was not as important as the non chiral catalysts employed in the microwave-assisted process. In any case, these findings were found to be in good agreement to previous reports by Ravasio *et al.* in which (−)-menthol could be achieved in high yields with high selectivities using Cu/SiO_2 catalysts.[18]

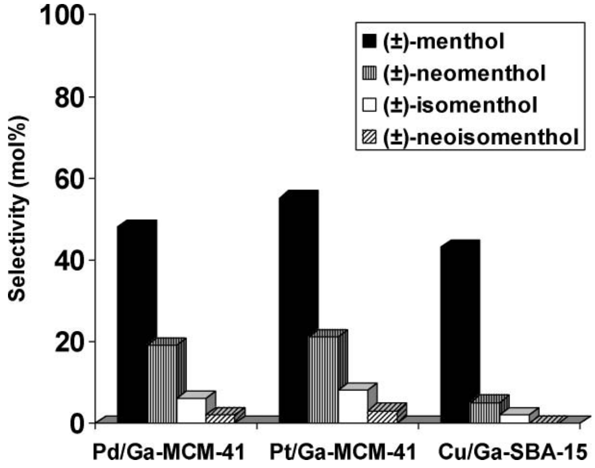


Fig. 2 Diastereoisomer distribution in the microwave-assisted tandem cyclisation/hydrogenation of (±)-citronellal to (±)-menthols using optimised catalytic systems. Reaction conditions: 10 mmol citronellal, 5 mL 2-propanol, 1 mmol K_2CO_3, 0.05 g catalyst, MW, 100 W, 120–130 °C (maximum temperature reached), 15 min reaction.

In any case, we were inspired by previous reports showing the addition of chiral modifiers including alkaloids (quinine, cinchonine, cinchonidine) could significantly improve selectivities and enantiomeric excess in asymmetric reactions including enantioselective hydrogenations.[20,21] We then devised a similar microwave protocol in which a chiral modifier [including quinine (QN), cinchonine (CN) and cinchonidine (CD)] was added to investigate its potential effect in the distribution of the diastereoisomers using enantiomerically pure (+)-citronellal as starting material. Results are summarised in Fig. 3. The addition of cinchonidine (CD) had a remarkable effect in the diastereoselectivity of the poor (−)-menthol systems, with a maximum of a 75% selectivity to the target menthol achieved with the 2% Pt/Ga-MCM-41 catalyst.

Further investigations are currently ongoing to unravel the involvement of the alkaloid in the microwave-assisted process to further extend the protocol to other chiral modifiers including quinidine, quinoline, lepidine, *etc.* and/or catalysts (*e.g.* supported nanoparticles on chitosan and other chiral supports).

The remarkable increase in (−)-menthol stereoselectivity found for CD might be related to the higher interaction of CD within the system due to its higher adsorption strength, in good agreement with previous reports.[22,23] More work is needed to verify and support these findings.

Conclusions

A simple, efficient and environmentally friendly one-step process has been developed for the microwave-assisted conversion of (±)-citronellal to (±)-menthols. (±)-Citronellal cyclisation to (±)-isopulegols is favoured on Lewis acid sites, while the presence

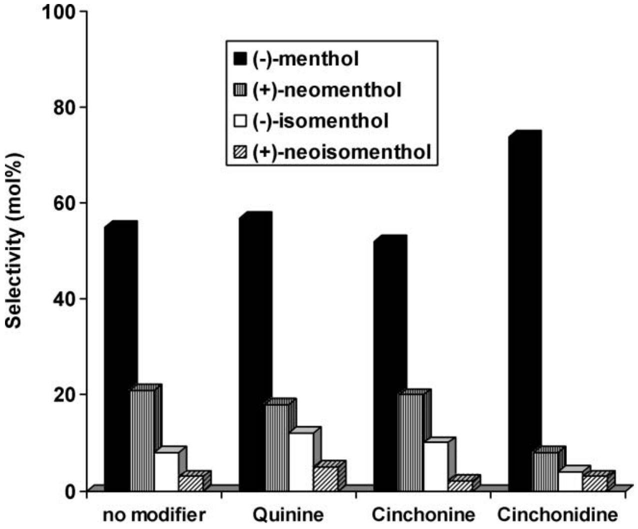


Fig. 3 Effect of the addition of chiral modifiers in the distribution of stereoisomers of the 2% Pt–Ga-MCM-41 catalysed production of menthols from (+)-citronellal. Reaction conditions: 10 mmol citronellal, 5 mL 2-propanol, 1 mmol K_2CO_3, 0.05 g catalyst, 0.008 g modifier (substrate/modifier 200 ratio), MW, 100 W, 120–130 °C (maximum temperature reached), 15 min reaction.

of supported nanoparticles under hydrogen transfer conditions (2-propanol + base) further promoted the subsequent hydrogenation of the double bond in isopulegols to (±)menthols. Reaction rates on both steps are improved under microwave irradiation to give high yields of menthols in short times of reaction (typically 15 min). 2% Pt–Ga-MCM-41 exhibited the optimum conversion and selectivity to menthols, combining high isopulegol yields (*via* Lewis promoted cyclisation) with the superior performance of Pt in the hydrogenation of the double bond to (±)-menthols.

When enantiomerically pure (+)-citronellal was employed as starting material instead of the racemic compound, a 55% maximum selectivity to (–)-menthol was observed. The addition of small quantities of a chiral modifier such as cinchonidine increased the selectivity to (–)-menthol up to a 75%. Supported nanoparticles on such mesoporous materials were also proved to be highly stable and reusable under investigated conditions, offering a potentially interesting alternative to the conventional production of these important natural products.

Acknowledgements

Authors gratefully acknowledge support from Ministerio de Ciencia e Innovación (Project CTQ2007-65754/PPQ). Rafael Luque is also grateful to Ministerio de Ciencia e Innovación for the concession of a Ramon y Cajal contract (RYC-2009-04199).

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