

Hydrogenation of (–)-menthone, (+)-isomenthone, and (+)-pulegone with platinum/tin catalysts

Virginia Vetere^a, Gerardo F. Santori^{a,b}, Albertina Moglioni^c, Graciela Y. Moltrasio Iglesias^c,
Mónica L. Casella^a, and Osmar A. Ferretti^{a,b,*}

^a CINDECA (UNLP-CONICET), 47 No. 257, (1900) La Plata, Argentina.

^b Facultad de Ingeniería de la UNLP, 47 No. 257, (1900) La Plata, Argentina.

^c Departamento de Química Orgánica, Facultad de Farmacia y Bioquímica, UBA,
Junín 954, (1113) Buenos Aires, Argentina.

Received 13 May 2002; accepted 13 September 2002

The hydrogenation of (–)-menthone, (+)-isomenthone, and (+)-pulegone over SiO₂-supported Pt and Pt–Sn catalysts was studied in this work. The modification with tin was performed by means of the techniques of surface organometallic chemistry on metals. This way of modifying the catalysts allowed stereoisomers of menthol to be obtained in a one-step process. The hydrogenation of these terpenes was favored by the presence of tin in the bimetallic phase.

KEY WORDS: hydrogenation; menthol isomers; platinum/tin catalysts; surface organometallic chemistry.

1. Introduction

The reduction of some natural terpenes allows the corresponding alcohols that are generally interesting in the chemical, pharmaceutical and food industries to be obtained. Menthols are found among these alcohols and are the reduction products of menthone. One of the most important of these alcohols is the (–)-menthol, which is produced worldwide on a scale of 4500 tonnes per year (1992), used in many consumer products such as, for example, cigarettes, chewing gum, toothpaste, pharmaceuticals, and personal care [1].

The main natural source of menthol is the essential oil of *Mentha arvensis*, which also contains high concentrations of menthone and pulegone. For this reason, it is of practical interest to study the hydrogenation of both compounds as a way to increase the production yield of menthols. Starting from the (+)-pulegone hydrogenation, a (–)-menthone and (+)-isomenthone mixture is obtained, which in turn produces four diastereomeric alcohols as reduction products: (+)-neomenthol, (–)-menthol, (+)-neoisomenthol, and (–)-isomenthol. Figure 1 shows the reaction scheme of these hydrogenations. The distribution of the menthol individual isomers varies depending on the applied reduction mode, the catalyst employed, and the reaction conditions [2,3].

(–)-Menthol can be synthesized through different routes: in the Takasago process, for instance, the

(–)-menthol production is carried out by enantioselective isomerization of geranyldiethylamine using optically active rhodium-BINAP catalyst. This stage generates an optical active enamine which, by hydrolysis, produces (+)-citronellal. An intramolecular ene reaction mediated by ZnBr₂ then gives (–)-isopulegol. Next, the unsaturated alcohol is separated from the reaction mixture and hydrogenated to (–)-menthol [4]. The production of important amounts of less useful by-products such as citronellol and geraniol is a disadvantage of this method. Synthetic (–)-menthol is produced on a commercial scale in Europe and the USA from m-cresol by alkylation with propene to thymol followed by its hydrogenation to a racemic menthol [5]. (–)-Menthol can also be obtained by hydrogenation of (–)-pulegone to (–)-menthone with Raney Ni as catalyst, and its subsequent reduction with NaBH₄ or Rh supported on SiO₂ or Al₂O₃ [6].

The classical methods to reduce ketones are based upon the use of metallic hydrides or Raney Ni. Catalytic systems that are able to hydrogenate carbonyl groups in a very efficient and selective manner have been developed by our research group [7,8]. These catalysts are based on platinum supported on silica modified by the addition of tin. Tin is introduced by using techniques derived from the so-called surface organometallic chemistry on metals (SOMC/M) that provides technical procedures to prepare catalytic systems in a controlled way [9–11].

In the present work, the hydrogenation of (–)-menthone, (+)-isomenthone and (+)-pulegone is studied using Pt/SiO₂ catalysts modified by tin in order to obtain menthols with high yield in a single-stage process.

* To whom correspondence should be addressed.
E-mail: ferretti@quimica.unlp.edu.ar

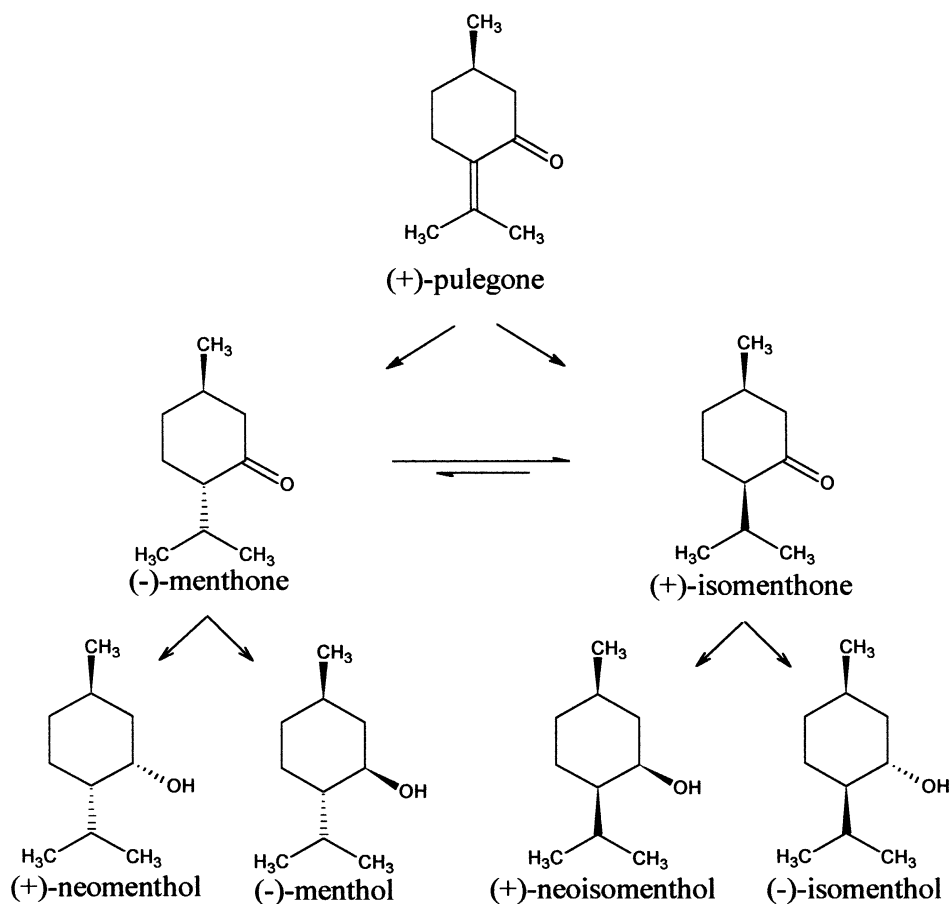


Figure 1. Reaction scheme for (+)-pulegone, (-)-menthone, and (+)-isomenthone hydrogenation.

2. Experimental

2.1. Catalyst preparation

A Degussa silica (Aerosil, 200 m² g⁻¹) was used as support. The silica was suspended in NH₄OH_(aq) under stirring prior to the addition of the [Pt(NH₃)₄]²⁺ solution, having a concentration so as to obtain 1% w/w Pt exchanged on the silica. The solid was kept under stirring for 24 h at 298 K and then the suspension was separated by filtration under vacuum. The solid was repeatedly washed, dried at 378 K, calcined in air at 773 K and reduced in flowing H₂ at the same temperature, leading to the monometallic Pt/SiO₂ catalyst. This catalyst was used for the preparation of PtSn systems.

Tin-modified catalysts were prepared by reaction of an SnBu₄ solution in *n*-decane with the reduced Pt/SiO₂ catalyst at 393 K under flowing H₂. After 4 h under reaction, the liquid phase was separated and the solid was repeatedly washed with *n*-heptane and subsequently dried in Ar at 363 K. The solids obtained after this procedure, identified as organobimetallic catalysts (PtSn-OM), still had butyl groups grafted to the surface. The bimetallic phases (PtSn-BM) were obtained by elimination of the organic groups by activation of PtSn-OM catalysts in flowing H₂ at 773 K for 2 h. Both

tin-modified catalysts had an Sn content equal to one, expressed as the Sn/Pt atomic ratio.

2.2. Catalyst characterization

The platinum and tin contents were determined by atomic absorption. H₂ and CO adsorption measurements were carried out in a volumetric apparatus. Samples were dried at 393 K in an He flow, reduced at 773 K under an H₂ flow for 2 h. The chemisorbed amount of H₂ or CO on the platinum surface (expressed as H/Pt and CO/Pt, respectively) was calculated by using the double isotherm method. The size distribution of metallic particles was determined by transmission electron microscopy (TEM) using a JEOL 2010 instrument. To estimate the mean particle size, the particles were considered spherical and the second moment of the distribution was employed.

XPS experiments were conducted on an ESCA 750 Shimadzu spectrometer equipped with a hemispherical electron analyzer and an Mg K_α (1252 eV) X-ray source. Fresh samples were mounted onto a manipulator which allowed the transfer from the preparation chamber into the analysis chamber. PtSn-OM samples were dried and PtSn-BM samples were reduced *in situ* at 673 K for 1 h. The binding energy (BE) of the C 1s

peak at 284.6 eV was taken as an internal standard. The intensities were estimated by calculating the integral of each peak after subtraction of the S-shaped background and by fitting the experimental peak to a Lorentzian/Gaussian mix of variable proportion. The atomic fraction determination of each species was carried out taking into account the signal intensity and the corresponding sensitivity factor [12].

2.3. Hydrogenation tests

The starting substrates in the hydrogenation reactions were (–)-menthone (Across), (+)-isomenthone (International Flavors and Fragrances), and (+)-pulegone (International Flavors and Fragrances). In the (–)-menthone hydrogenation, the starting substrate had a composition of 80% (–)-menthone:20% (+)-isomenthone determined by GLC, whereas the starting material in the (+)-isomenthone hydrogenation had a composition of 90% (+)-isomenthone:10% (–)-menthone.

The hydrogenation reactions in liquid phase were performed in a batch reactor at 1.0 MPa of H₂ and 388 K, employing 0.25 g of catalyst. The ketones were introduced in the stirred reactor (800 rpm) dissolved in *n*-dodecane (0.25 ml ketone/60 ml *n*-dodecane). The reaction progress was followed by sampling a sufficient number of microsamples. The composition of the samples was analyzed by means of a Varian GC 3400 gas chromatograph, equipped with a 30 m DB-wax capillary column and a flame ionization detector. The products obtained were optically pure (+)-neomenthol, (–)-menthol, (+)-neoisomenthol, and (–)-isomenthol, analyzed by GC in a CP-Chirasil-Dex CB capillary column. Reaction products were identified by means of GC/MS.

Pt/SiO₂ and PtSn-BM catalysts were pre-treated under flowing H₂, increasing the temperature from ambient to 773 K, and holding it for 2 h. PtSn-OM catalysts were prepared and tested in the same reactor to prevent any contact with the atmosphere.

The homogeneous reduction of the substrates was carried out by dissolving 6 mmol of each terpenone (pulegone, menthone, isomenthone) in 15 ml methanol and carefully adding 1.2 g of NaBH₄. The mixture was heated under reflux for 3.5 h, with continuous stirring.

Then it was allowed to cool down to ambient temperature and it was diluted with 25 ml of water. Extraction with ether was carried out with the purpose of separating the organic phase, which was then dried on anhydrous Na₂SO₄. This phase was concentrated under vacuum, and in this way the corresponding alcohols were obtained. The products of these reactions were analyzed by ¹H NMR (on a Bruker 300 spectrometer in Cl₃CD).

3. Results and discussion

3.1. Characterization

Characterization results of the studied catalysts are shown in table 1. The monometallic catalyst Pt/SiO₂ presents a homogeneous distribution of the particle size between 1 and 3 nm, and an H/Pt ratio near 0.6, indicating a high dispersion of the metallic phase. Tin addition *via* SOMC/M produces a slight increase of the particle size which should not be assigned to the platinum sintering, but to a selective tin deposit on it [13]. At the same time, the H(CO)/Pt value diminishes to *ca.* 0.2. Taking into account that tin is a metal not able to chemisorb H₂ or CO, the values of the chemisorbed gas by this phase demonstrate that an appreciable amount of superficial platinum is still present, enough for the catalytic activation in the hydrogenation reactions in which the catalyst is employed.

With respect to platinum, in the region corresponding to Pt 4f_{7/2}, one peak appears at around 71 eV indicating its complete reduction. An interesting aspect arises from the analysis of BE values of platinum shown in table 1. In the systems modified by tin, a shift is observed in the BE toward lower values of approximately 1 eV with respect to Pt/SiO₂. This shift can be interpreted as an electronic transfer from tin to platinum. These modifications strengthen the hypothesis of the electronic effects induced by tin in agreement with chemisorption results.

Table 1 shows the results for XPS Sn 3d_{5/2} line for both PtSn-OM and PtSn-BM catalysts. The deconvolution of the spectra allowed one to obtain the contribution of the different tin species in each sample, as is shown in this table. The PtSn-OM catalyst has a stoichiometry Pt[SnBu_{2.5}]_{1.0}/SiO₂ and, according to XPS measurements, tin is present as Sn(0) and Sn(II,IV) in similar

Table 1
Characterization by XPS and chemisorption of H₂ and CO of the Pt/SiO₂, PtSn-BM, and PtSn-OM catalysts.

Catalyst	Global stoichiometry of the active phase	Pt content (wt%)	Sn/Pt	H/Pt	CO/Pt	Binding energy (BE)			Sn(0)/[Sn(0) + Sn(II, IV)]
						Pt 4f _{7/2}	Sn(0) 3d _{5/2}	Sn(II, IV) 3d _{5/2}	
Pt/SiO ₂	Pt	1.0	–	0.65	0.55	71.6	–	–	–
PtSn-OM	Pt[SnBu _{2.5}] _{1.0}	1.0	1.0	n.d.	n.d.	70.8	484.3	487.0	0.45
PtSn-BM	PtSn _{1.0}	1.0	1.0	0.20	0.25	70.6	484.6	487.1	0.64

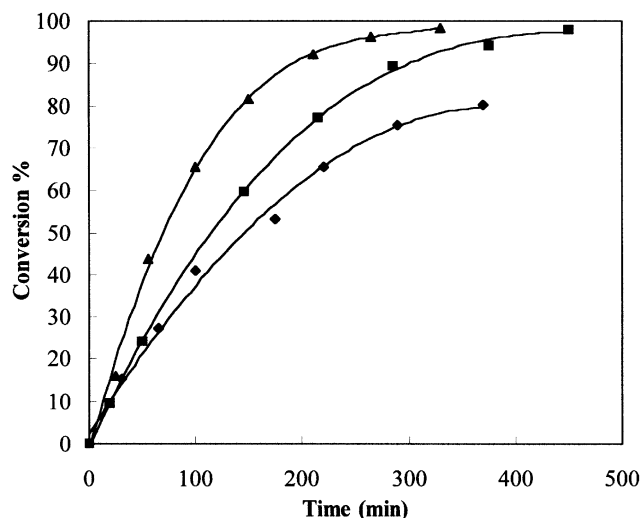


Figure 2. Conversion of (–)-menthone as a function of time for (◆) Pt/SiO₂, (■) PtSn-BM, and (▲) PtSn-OM catalysts.

proportions. In the system denominated PtSn-BM, approximately 65% of the tin is found as Sn(0) and the rest as ionic tin (Sn(II,IV)).

3.2. Hydrogenation of (–)-menthone and (+)-isomenthone

Figure 2 shows the variation of (–)-menthone conversion as a function of time for Pt/SiO₂, PtSn-BM, and PtSn-OM catalysts. The curves corresponding to Pt/SiO₂ catalyst show a slight flattening, indicating a certain deactivation process, analogous to what has been observed for other carbonyl compounds, assigned to the formation of oligomers, accepting that the global reaction order with respect to the substrate is zero or near zero [14,15]. The tin presence seems to improve the stability of the catalytic systems. With respect to the initial reaction rate, the obtained values were quite similar for the three studied catalysts: 0.10, 0.09, and 0.15 mmol (g_{Pt}s)^{–1}, for Pt/SiO₂, PtSn-BM and PtSn-OM, respectively.

The hydrogenation products of menthone are (+)-neomenthol, (–)-menthol (main products), (+)-neo-isomenthol, and (–)-isomenthol (minor products). The

existence of these minor products can be awarded to the (+)-isomenthone presence in the reaction mixture. (–)-Menthone is very susceptible to epimerization, changing the configuration of the carbon atom neighboring the carbonyl group, originating from (+)-isomenthone. The configuration in the second asymmetric center of the (–)-menthone is preserved, and thus no racemization occurs [16]. Table 2 shows the selectivity toward the individual isomeric alcohols, measured at conversion values of 20 and 80%, for all the studied catalysts. As can be observed, the selectivity does not vary with the conversion, confirming that the menthols formed do not suffer any isomerization process.

As has been previously mentioned, in tin-modified catalysts the shift in the BE of Pt 4f_{7/2} toward lower values with respect to Pt/SiO₂ can be interpreted as an electronic transfer from tin to platinum. For this reason, it is acceptable to propose that polarized states of Pt^{δ–} and Sn^{δ+} are generated, which would be important in the (–)-menthone chemisorption through the negatively polarized oxygen atom. This adsorption mode would be responsible for the existence of a carbocationic intermediate, which would give place to an increase of (+)-isomenthone from (–)-menthone, and, as a consequence, to a higher proportion of (+)-neo-isomenthol, one of its hydrogenation products. This fact could explain the (–)-menthol presence as the main product of the (–)-menthone hydrogenation, with important (+)-neomenthol amounts.

The results presented here are significantly different from some previously published. Kukula and Červený, using Raney Ni catalysts, present results according to which the formation of isomeric menthols with axial hydroxyl group is markedly preferential, resulting in the formation of (+)-neomenthol and (+)-neo-isomenthol in amounts higher than 80% [3]. Our results could show that, for the platinum-based systems studied in this work, the (–)-menthone molecule probably approaches the catalyst surface in parallel orientation with the isopropyl group pointing towards the catalyst. In this way, the (–)-menthone molecule could form an adsorption complex in which the oxygen atom is more reactive, because it is negatively polarized. Oxygen could react with a hydrogen atom before the carbon

Table 2
Hydrogenation of (–)-menthone. Selectivity^a towards isomeric menthols, measured at two different levels of conversion.

Conversion (%)	(+)–Neomenthol (%)		(+)–Neo-isomenthol (%)		(–)-Menthol (%)		(–)-Isomenthol (%)	
	X = 20	X = 80	X = 20	X = 80	X = 20	X = 80	X = 20	X = 80
Pt/SiO ₂	42	39	10	9	53	50	3	2
PtSn-OM	36	37	19	19	41	44	2	0
PtSn-BM	37	38	16	18	40	44	2	0
NaBH ₄	47	47	10	10	43	43	0	0

^a Selectivity % = $n_i/n_t \times 100$. n_i = number of moles of product i . n_t = total number of moles.

Table 3
Hydrogenation of (+)-isomenthone. Selectivity^a towards isomeric menthols, measured at 25% conversion.

	(+)-Neomenthol (%)	(+)-Neoisomenthol (%)	(–)-Menthol (%)	(–)-Isomenthol (%)
Pt/SiO ₂	9	75	10	6
PtSn-OM	8	85	6	1
PtSn-BM	6	90	3	1
NaBH ₄	7	86	6	1

^a Selectivity % = $n_i/n_t \times 100$. n_i = number of moles of product i . n_t = total number of moles.

atom of the carbonyl group could, generating (–)-menthol, with the hydroxyl group in an equatorial position.

Results of the (+)-isomenthone hydrogenation with the three studied catalysts are presented in table 3 and figure 3. The main product in every case proved to be (+)-neoisomenthol, which can be explained taking into account the steric control of this reaction that arises from the *cis* relationship of its methyl and isopropyl groups.

With regard to the reaction rate, for the three studied catalysts, the (+)-isomenthone hydrogenation proceeds at a lower rate than that of the (–)-menthone. The initial rate values were 0.01, 0.03, and 0.07 mmol (g_{Pt}s)^{–1}, for Pt/SiO₂, PtSn-BM, and PtSn-OM, respectively. The reaction-rate increase observed for the tin-modified systems is again evidence of the effects of their electronic nature due to the presence of ionic tin (XPS data in table 1), just as happens with other substrates, like cinnamaldehyde and benzaldehyde [7,14].

In tables 2 and 3, reduction results of (–)-menthone and (+)-isomenthone with NaBH₄ are also presented. The basic characteristics of NaBH₄, which acts donating a hydride ion, do not contribute to the isomerization of (–)-menthone to (+)-isomenthone. Consequently, both for (–)-menthone and (+)-isomenthone, the distribution of products is closer to that obtained in

the hydrogenation with the Pt/SiO₂ catalyst than to that achieved with the PtSn-BM and PtSn-OM catalysts.

3.3. Hydrogenation of (+)-pulegone

Results of the (+)-pulegone conversion as a function of time are shown in figure 4. The pulgone molecule contains two conjugated double bonds, C=C and C=O; as is well known, the C=C bond hydrogenation is thermodynamically favored when supported metallic catalysts are used [17]. In accordance with this, the Pt/SiO₂ catalyst shows a high rate of C=C bond hydrogenation, obtaining a (+)-pulegone conversion of 100% in 65 min of reaction.

Figure 5 shows the composition of the reaction products obtained when using Pt/SiO₂ catalyst in the (+)-pulegone hydrogenation. In the first step, the C=C bond hydrogenation takes place to give a (–)-menthone and (+)-isomenthone mixture having a composition of practically 50% each. Once (+)-pulegone has almost been consumed, the subsequent (–)-menthone and (+)-isomenthone hydrogenation proceeds very slowly, with production of isomeric menthols. As can be observed in figure 5, after approximately 12 h, the reaction reaches a plateau at *ca.* 35% conversion of (–)-menthone and (+)-isomenthone to the isomeric menthols. At this reaction time, the mixture composition is: 28%

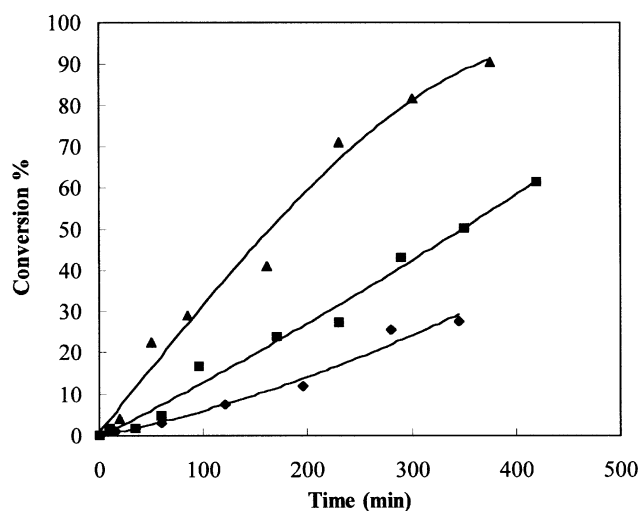


Figure 3. Conversion of (+)-isomenthone as a function of time for (♦) Pt/SiO₂, (■) PtSn-BM, and (▲) PtSn-OM catalysts.

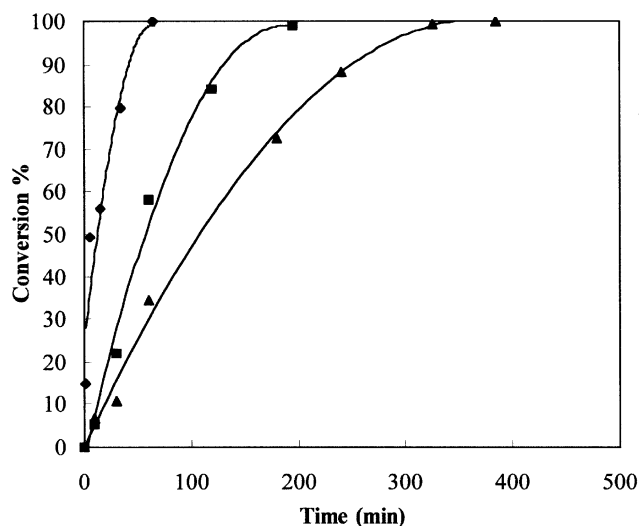


Figure 4. Conversion of (+)-pulegone as a function of time for (♦) Pt/SiO₂, (■) PtSn-BM, and (▲) PtSn-OM catalysts.

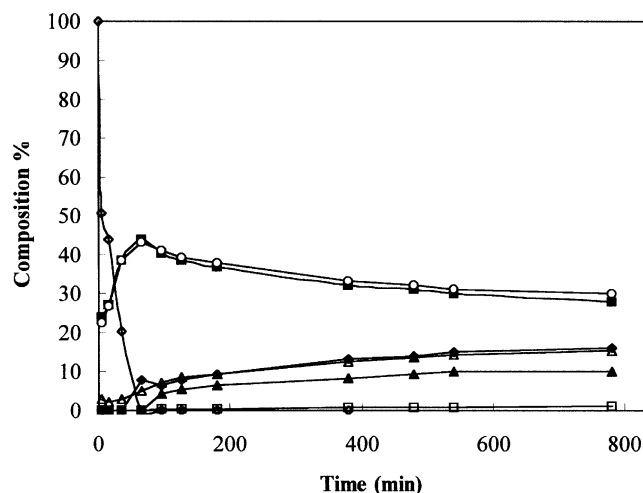


Figure 5. Product distribution (mol%) during the course of (+)-pulegone hydrogenation on Pt/SiO₂ catalyst: (◇) (+)-pulegone, (■) (–)-menthone, (○) (+)-isomenthone, (Δ) (+)-neomenthol, (▲) (–)-menthol, (◆) (+)-neoisomenthol, and (□) (–)-isomenthol.

(–)-menthone, 30% (+)-isomenthone, 15% (+)-neomenthol, 16% (+)-neoisomenthol, 10% (–)-menthol, and 1% (–)-isomenthol. These results indicate a lower transformation rate of (–)-menthone and (+)-isomenthone to menthols in comparison with that previously obtained when using (–)-menthone and (+)-isomenthone as isolated starting substrates. This fact would indicate that, starting from (+)-pulegone, a higher poisoning degree of the catalytic surface is observed causing a modification in the architecture of the active sites.

When studying the (+)-pulegone hydrogenation using tin-modified platinum catalysts, the behavior is completely different to that observed for the hydrogenation of other substrates containing C=O and C=C conjugated bonds. In α,β -unsaturated aldehydes, the effect of tin is a combination of geometric and electronic aspects that enhance the C=O bond hydrogenation, with simultaneous inhibition of the C=C bond hydrogenation [7,8]. According to this, in the case of (+)-pulegone, the main product of its hydrogenation should be *cis* (–)-pulegol. However, this product has not been detected in any of the experiments carried out with the tin-modified catalysts presented here. Other research works that are being carried out at our laboratory with other α,β -unsaturated ketones show this same type of behavior [18], *i.e.*, contrary to what happens with the α,β -unsaturated aldehydes, in the case of the ketones, the C=C bond is preferably hydrogenated, even in the presence of PtSn catalysts.

When tin-modified catalysts are used, the primary products of the (+)-pulegone hydrogenation are, as in the case of Pt/SiO₂, (–)-menthone and (+)-isomenthone. As is observed in figure 5, the (+)-pulegone consumption rate for PtSn-BM and PtSn-OM catalysts is lower than that corresponding to Pt/SiO₂.

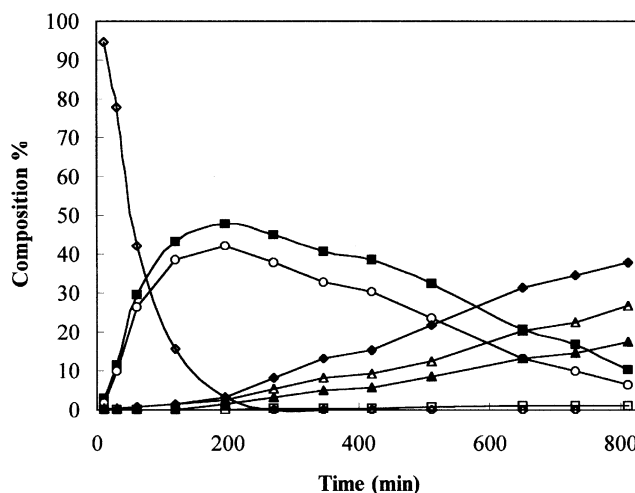


Figure 6. Product distribution (mol%) during the course of (+)-pulegone hydrogenation on PtSn-BM catalyst: (◇) (+)-pulegone, (■) (–)-menthone, (○) (+)-isomenthone, (Δ) (+)-neomenthol, (▲) (–)-menthol, (◆) (+)-neoisomenthol, and (□) (–)-isomenthol.

Figures 6 and 7 present the results of the distribution of products for the (+)-pulegone hydrogenation as a function of the reaction time, for PtSn-BM and PtSn-OM catalytic systems. A very interesting aspect to point out is that tin-modified catalysts are able to carry out both hydrogenation steps with good yield to menthols, the opposite of what happens with Pt/SiO₂ catalyst. It is important to point out that in this case the hydrogenation of (–)-menthone and (+)-isomenthone is slower than when starting from the pure substrates (figures 2 and 3). These results could be assigned to the higher poisoning of the catalytic surface in the presence of (+)-pulegone, probably due to the formation of oligomers, since hydrogenation experiments carried out with equimolar mixtures of (–)-menthone and (+)-isomenthone (free of pulegone) do not show the same phenomenon.

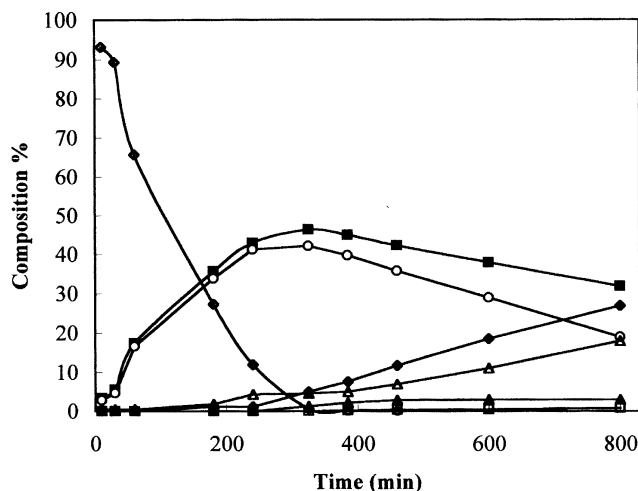


Figure 7. Product distribution (mol%) during the course of (+)-pulegone hydrogenation on PtSn-OM catalyst: (◇) (+)-pulegone, (■) (–)-menthone, (○) (+)-isomenthone, (Δ) (+)-neomenthol, (▲) (–)-menthol, (◆) (+)-neoisomenthol, and (□) (–)-isomenthol.

Table 4
Hydrogenation of (+)-pulegone. Product distribution (mol%) after 12 h of reaction.

	Pt/SiO ₂	PtSn-OM	PtSn-BM	NaBH ₄
(–)-Menthone %	28	32	10	0
(+)-Isomenthone %	30	19	6	0
(+)-Neomenthol %	15	18	27	2
(+)-Neoisomenthol %	16	27	38	9
(–)-Menthol %	10	3	17	2
(–)-Isomenthol %	1	1	1	0
<i>cis</i> (–)-Pulegol %	0	0	0	86

Results of the distribution of products obtained after 12 h of reaction are shown in table 4 for all the studied catalysts. The stereoselectivity in this case is very different from that obtained in the (–)-menthone hydrogenation. Results depicted in table 4 are similar to those found in the literature [3]. Again, the poisoning due to the pulegone presence could lead to modifications in the catalytic surface: the active sites contaminated by the probable formation of oligomers during the first reaction phase (hydrogenation of (+)-pulegone to menthone/isomenthone) are of a different nature for the consecutive reaction toward menthols. This difference in the active site architecture found by menthone and isomenthone molecules for the second hydrogenation step would be responsible for the changes observed in the stereoselectivity. Deeper investigations are necessary to understand the role that the catalyst plays in the (+)-pulegone hydrogenation.

Results of the (+)-pulegone reduction with NaBH₄ are presented in table 4. As can be observed, there exists a great difference among these results and those obtained when using platinum-based heterogeneous catalysts. When carrying out the (+)-pulegone reduction with NaBH₄ the main product turns out to be *cis* (–)-pulegol, with just a small menthol content, even after 18 h of reaction.

4. Conclusions

The hydrogenation study of (–)-menthone, (+)-isomenthone, and (+)-pulegone using PtSn-BM and PtSn-OM catalysts prepared *via* SOMC/M shows that menthols may be obtained in a one-stage process.

The (–)-menthone hydrogenation with platinum-based catalysts, contrary to what happens with other catalytic systems, generates (–)-menthol as the main product, together with important (+)-neomenthol amounts. The presence of tin favors this reaction rate.

The (+)-isomenthone hydrogenation with platinum-based catalysts generates (+)-neoisomenthol as the

main product, a result that can be explained taking into account the steric control of this reaction.

The use of platinum-based heterogeneous catalysts allows the (+)-pulegone hydrogenation to isomeric menthols. The presence of tin increases the yield to menthols. On the contrary, when using NaBH₄ to reduce (+)-pulegone, *cis* (–)-pulegol is obtained as the main product.

Acknowledgments

This work was supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Agencia Nacional de Promoción Científica y Técnica PICT 98 No. 14-04378, Argentina. XPS experiments were performed at CENACA (Centro Nacional de Catálisis), Santa Fe (Argentina) with equipment donated by JICA (Japan International Cooperation Agency).

References

- [1] A.N. Collins, G.N. Sheldrake and J. Crosby, *Chirality in Industry* (Wiley, Chichester, 1992).
- [2] A. Tungler, T. Máthé, Z. Bende and J. Petro, *Appl. Catal.* 19 (1985) 365.
- [3] P. Kukula and L. Červený, *Appl. Catal. A: Gen.* 193 (2000) 285.
- [4] M. Misono and N. Nojiri, *Appl. Catal.* 64 (1990) 1.
- [5] Boelens Aroma Chemical Information Service (BACIS), The Netherlands (1996).
- [6] P. Ravi, R. Ravichandran and S. Divakar, *J. Mol. Catal.* 148 (1999) 145.
- [7] G. Santori, M. Casella, G. Siri, O. Ferretti, A. Moglioni and G. Moltrasio, *Stud. Surf. Sci. Catal.* 130 (2000) 2063.
- [8] G.F. Santori, M.L. Casella, G.J. Siri, H.R. Adúriz and O.A. Ferretti, *Appl. Catal. A: Gen.* 197 (2000) 141.
- [9] J. Margitfalvi, M. Hegedűs, S. Göbölös, E. Kern-Tálas, P. Szedlaczek, S. Szabó and F. Nagy, *Proc. 8th Int. Congr. Catal. Berlin, 1984*, vol. 4, p. 903.
- [10] O.A. Ferretti, Bettega de Pauli, J.P. Candy, G. Mabilon and J.P. Bournonville, *Stud. Surf. Sci. Catal.* 31 (1987) 713.
- [11] J.P. Candy, O. Ferretti, J.P. Bournonville, A. El Mansour, J. Basset and G. Martino, *J. Catal.* 112 (1988) 210.
- [12] C.D. Wagner, W.M. Riggs, L.E. Davies and J.F. Moulder, *Handbook of X-Ray Photoelectron Spectroscopy*, ed. G.E. Muilemberg (Minneapolis, USA, 1978).
- [13] G.F. Santori, M.L. Casella, G.J. Siri, H.R. Adúriz and O.A. Ferretti, *React. Kinet. Catal. Lett.* 75 (2002) 225.
- [14] G. Santori, M. Casella and O. Ferretti, *J. Mol. Catal. A: Chemistry* 186 (2002) 223.
- [15] R.M. Makouangou, D.Y. Murzin, A.E. Dauscher and R.A. Touroude, *Ind. Eng. Chem. Res.* 33 (1994) 1881.
- [16] E. Eliel, S. Wilen and L. Mander, *Stereochemistry of Organic Compounds* (Wiley, 1994).
- [17] P. Gallezot and D. Richard, *Catal. Rev. Sci. Eng.* 40 (1988) 81 and references therein.
- [18] V. Vetere, G. Santori, A. Moglioni, G. Moltrasio, M. Casella and O. Ferretti, to be published.