

Stereoselective hydrogenation of terpenes using platinum-based catalysts

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Abstract

In the present paper, the catalytic hydrogenation of some terpenes is discussed. Catalysts employed were silica supported Pt and Pt modified by tin addition using techniques derived from surface organometallic chemistry on metals. Selected substrates were α -pinene, verbanone, fenchone, camphor and verbenone. The catalytic systems studied allow the control of reaction stereoselectivity. The hydrogenation of α -pinene led selectively to *cis*-pinane, and it was possible to observe that the modification of Pt/SiO₂ with Sn caused an important decrease of the catalytic activity; this fact can be explained by combined electronic and geometrical effects. In sterically hindered terpenones (fenchone and camphor), the topography of the molecule resulted of fundamental importance in controlling the stereoselectivity of the reaction. In verbenone hydrogenation, the Pt/SiO₂ catalyst allowed to obtain *cis*-verbanone with high yield and catalysts modified with Sn led to the formation of a principal product (*cis*-verbanol) different than the one obtained by chemical reduction with NaBH₄ (*cis*-verbenol).

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1. Introduction

The traditional way to obtain fine chemicals and specialties has been a non-catalytic organic synthesis route. Nevertheless, in the last years the application of catalytic methods has increased due to the growing importance of production costs, waste minimization and also because of the requirements of new selectivities, such as chemo-, stereo- and enantioselectivities [1,2]. For instance, catalytic conversion of terpenes and derivatives, represents an attractive way for the synthesis of medicines, fragrances, cosmetic bases and vitamins [3–8]. As an example, verbanol is a key compound for the production of fragrances, like 3,4,6-trimethylhept-5-enal with a strong lemon aroma [9]; verbanol can be obtained through the hydrogenation of verbenol prepared by α -pinene oxidation [10]. Likewise,

many other valuable intermediate or final products may be obtained by the catalytic hydrogenation of terpenes.

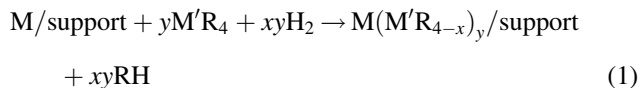
Supported metallic catalysts are active for hydrogenation reactions, but, very often their properties (selectivity, stability) have to be improved, for instance, by the addition of a second metal [11–15]. Although there are many procedures to prepare bimetallic catalysts, the necessity of using controlled preparation techniques is evident nowadays. Among these techniques, Surface Organometallic Chemistry on Metals (SOMC/M) is a good method to selectively add a second metal onto a first supported one [16–18]. The resulting catalytic system can achieve high activities and selectivities in many reactions. The reaction of an organometallic compound of the type M'R₄ (M': Sn, Ge, Pb; R: methyl, butyl, phenyl, menthyl) with a supported transition metal M (M: Ni, Rh, Pt, etc.) leads to the generation of different phases, all of them with interesting catalytic properties in many hydrogenation reactions:

- (i) In a first step, the M'R₄ compound is made to react with the monometallic catalyst M/support (support: SiO₂, γ -Al₂O₃,

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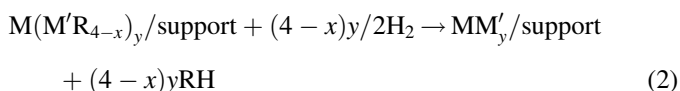
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MCM-41, etc.) under a H₂ atmosphere and temperatures between 333 and 423 K. The following equation represents this step:



the reaction product is denominated MM'–OM catalyst.

(ii) The organometallic MM'–OM catalyst loses all the organic fragments by heating at 773 K under H₂, leading to a bimetallic catalyst (MM'–BM), which displays catalytic properties completely different from those of the starting monometallic phase. This step can be represented by the following equation:



According to the M'R₄ concentration and to the reaction temperature, the value of *x* ranges between 0 and 4, for *y* ≤ 2 [13].

This contribution reports the performance of Pt and Sn-modified Pt catalysts in the hydrogenation of terpenes. The tin addition is carried out by means of SOMC/M techniques. Special emphasis is given to the product distribution and stereoselectivity obtained.

2. Experimental

2.1. Catalyst preparation

A Degussa silica (Aerosil 200, 200 m² g⁻¹) was used as support. The silica was suspended in NH₄OH_(aq) under stirring prior to the addition of a [Pt(NH₃)₄]Cl₂ 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.

Sn-modified Pt catalysts were prepared with a Sn/Pt atomic ratio of 1. Sn was introduced by means of Surface Organometallic Chemistry on Metals (SOMC/M) techniques. To obtain PtSn–OM catalysts, a portion of reduced Pt/SiO₂ was reacted with tetra-*n*-butyltin in *n*-decane solution under H₂ atmosphere at 393 K. After 4 h reaction, the liquid phase was separated and the solid was repeatedly washed with *n*-heptane and subsequently dried in Ar at 363 K. The solid obtained after this procedure, identified as PtSn–OM, still had butyl groups anchored to the surface [13]. The bimetallic catalyst PtSn–BM was obtained by following the same procedure, eliminating the organic moieties by activation of PtSn–OM catalyst in flowing H₂ at 773 K for 2 h. The variation of SnBu₄ concentration and the amount of hydrocarbons evolved during the preparation reaction were analyzed using a Varian 3400 CX gas chromatograph equipped with a flame ionization detector, employing a 10% OV-101 column (1/8 in. i.d., 0.5 m length). Before their use, Pt/SiO₂ and PtSn–BM catalysts were treated under flowing H₂, increasing the

temperature from room to 773 K, and holding it for 2 h. PtSn–OM catalysts were tested without any further treatment after preparation, and handled without exposition into the air.

2.2. Catalyst characterization

The contents of Pt and Sn were determined by atomic absorption. Hydrogen chemisorption was measured in a static volumetric apparatus at room temperature for Pt/SiO₂ and PtSn–BM samples. For each of them, a first hydrogen adsorption isotherm was obtained for the sample previously reduced at 773 K for 4 h and then evacuated at the same temperature overnight. After the first isotherm, the sample was evacuated at room temperature and a second isotherm was carried out in the same manner. The difference between the two isotherms extrapolated to zero pressure gave the amount of the irreversibly adsorbed H₂. H/Pt values were calculated assuming an adsorption stoichiometry of unity.

The size distribution of metallic particles was determined by transmission electron microscopy (TEM) using a Jeol 100CX instrument. The samples were ground and ultrasonically dispersed in distilled water. Particles were considered spherical and the second moment of the distribution was used to estimate the mean particle size.

XPS analyses were obtained with an ESCA 750 Shimadzu spectrometer equipped with a hemispherical electron analyzer and a Mg Kα (1253.6 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 sample was dried and Pt/SiO₂ 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 fitting the experimental peak to a Lorentzian/Gaussian mix of variable proportion.

2.3. Hydrogenation reactions

The catalytic hydrogenation of α-pinene, verbanone, fenchone, camphor and verbenone was carried out in a stirred autoclave type reactor at 1 MPa of H₂ pressure and 353 K, using 0.25 g of catalyst, and *n*-decane as solvent. The substrate amount used in each test was 6.6 mmol/g of catalyst. The course of the reaction was followed by gas chromatography in a GC Varian 3400 chromatograph equipped with a capillary column of 30 m DB-WAX and a FID detector. The identification of the diverse reaction products was achieved by GC/MS in a Shimadzu QP5050 equipment. For verbenone and α-pinene, the products were identified by their ¹H NMR spectra, recorded on a Bruker 400 spectrometer and are reported as δ values. The other products were identified by comparison with those of authentic samples obtained by chemical reduction of the corresponding terpenones. The chemical reduction of the terpenones (6 mmol) was carried out in methanol (15 mL) with NaBH₄ (1.2 g) as reducing agent for 4 h at reflux (338 K). In all the cases the main product was the corresponding alcohol,

obtained as an oil. The products of the diverse reactions were identified through their ^1H NMR spectra (recorded on a Bruker 400 spectrometer) and are reported as δ values.

2.3.1. Verbanone

^1H NMR (δ ppm): 0.95 (3H, s), 1.12 (3H, d, $J = 8$ Hz), 1.30 (3H, s), 1.37 (1H, d, $J = 11$ Hz), 2.05–2.15 (2H, m), 2.35 (1H, m), 2.50–2.60 (2H, m), 2.85 (1H, dd, $J = 11$ and 20 Hz). ^{13}C NMR (δ ppm): 21.6, 25.2, 27.6, 29.0, 31.6, 40.8, 42.0, 48.0, 58.6, 215.0.

2.3.2. (1S)-(–)-Cis-pinane

^1H NMR (δ ppm): 0.85 (1H, dd, $J = 16$, $J = 6$), 0.97 (3H, s), 1.0 (3H, d, $J = 7$), 1.17 (3H, s), 1.40 (1H, m), 1.72 (1H, m), 1.75–1.92 (4H, m), 2.12 (1H, m), 2.29 (1H, m).

2.3.3. (+/–)-Exo-borneol

It was obtained in a 5:1 ratio (*exo*-borneol:*endo*-borneol) from reduction of racemic camphor. ^1H NMR of *exo*-borneol (δ ppm): 0.82 (3H, s), 0.91 (3H, s), 1.03 (3H, s), 1.50 (1H, m), 1.60–1.80 (6H, m), 3.65 (1H, m).

2.3.4. (+/–)-Endo-fenchol

It was obtained as a sole product from reduction of racemic fenchone. ^1H NMR (δ ppm): 0.87 (3H, s), 1.02 (3H, s), 1.05 (1H, m), 1.13 (3H, s), 1.30–1.50 (3H, m), 1.50–1.70 (3H, m), 3.25 (1H, s).

2.3.5. S-Cis-verbenol

It was obtained as a sole product from reduction of *S*-verbenone. ^1H NMR (δ ppm): 1.10 (3H, s), 1.30 (3H, s), 1.70 (3H, s), 1.80 (1H, m), 1.95 (1H, m), 2.30 (1H, m), 2.45 (1H, m), 4.50 (1H, s), 5.30 (1H, s).

2.3.6. S-Cis-verbanol

It was obtained as a sole product from reduction of *S*-verbanone. ^1H NMR (δ ppm): 1.15 (1H, m), 1.20 (3H, d, $J = 8$ Hz), 1.20 (3H, s), 1.30 (3H, s), 1.85 (1H, m), 2.00–2.20 (2H, m), 2.30–2.40 (1H, m), 2.50–2.60 (1H, m), 4.25 (1H, m).

3. Results and discussion

Catalysts were characterized by different techniques such as transmission electron microscopy (TEM), H_2 adsorption and X-ray photoelectron spectroscopy (XPS) as it is shown in Table 1.

Results obtained from TEM characterization can be summarized as follows: the global dispersion of the supported metallic phase is not practically affected by the Sn addition; the

particle size distribution is similar to the one of the monometallic system; the increase in the average size of metallic particles is slight and according to what is expected, by the selective addition of Sn atoms on metallic Pt. These results go in the direction of confirming that Sn is deposited specifically on the superficial platinum atoms, as it is mentioned in the literature for other systems prepared by SOMC/M (for example, for RhSn/SiO₂, it was verified by STEM that the signals of X fluorescence of Rh and Sn were always associated [19,20]). Values corresponding to the hydrogen chemisorption measured for bimetallic catalysts show a strong decrease in the amount of adsorbed hydrogen. This cannot be explained by a dispersion decrease by sintering of the metallic phase according to TEM results and can be attributed to geometric modifications of the base metal (Pt), due to the physical blocking by tin.

The XPS analysis of Pt/SiO₂ and tin modified catalysts presented a single peak in the region corresponding to Pt 4f signal. This indicates a complete reduction of the metallic phase. This result is in agreement with a previous work on PtSn catalysts prepared via SOMC/M (Sn/Pt = 0.4–0.7). In this work it was possible to demonstrate by means of EXAFS/XANES studies that there exists a single peak corresponding to the Pt–Pt distance (2.6 Å), indicative of reduced Pt forming metallic particles; likewise, the coordination number obtained resulted to be lower than the one corresponding to Pt “bulk”, due to the small size of metallic particles [21].

The Sn addition has an influence on the Pt structure, as it can be observed in Table 1. Thus, in the systems modified by Sn, the XPS signal of Pt presented a shift in the BE value of about 0.7–1 eV below the value corresponding to Pt/SiO₂. In both systems, PtSn–BM and PtSn–OM, the analysis of the region corresponding to Sn signal shows the presence of two peaks assigned to Sn(0) (BE around 484.5 eV) and Snⁿ⁺ (BE around 487.0 eV), respectively. The Sn(0) presence induces us to think about the formation of PtSn alloys. In an EXAFS study concerning this type of catalysts, in the case of the PtSn–OM system, no evidence of alloy formation was found; however, in PtSn–BM systems, the presence of two peaks was observed and was assigned to the existence of PtSn alloys [21]. From these results and the ones of literature, Scheme 1 is proposed for the representation of the catalytic systems studied in this work.

From Scheme 1, the following images can be proposed for the Sn-modified platinum-based catalytic phases: (i) in the PtSn–OM catalyst, butyl groups remain anchored on the surface with Sn present both as Sn(0) and Snⁿ⁺ in similar proportion and Pt atoms are found isolated by “islands” of PtSnBu_x fractions; (ii) in the PtSn–BM catalyst, part of Pt is alloyed with the metallic Sn and the remainder is isolated by such alloys. A

Table 1
Hydrogen chemisorption and TEM and XPS characterization of the catalysts used in this work

Catalyst	Sn/Pt	H/Pt	d_{TEM} (nm)	Binding energies (eV)			Sn ⁰ /(Sn ⁰ + Sn ⁿ⁺)
				Pt 4f _{7/2}	Sn(0) 3d _{5/2}	Sn ⁿ⁺ 3d _{5/2}	
Pt/SiO ₂	0	0.64	2.4	71.6	–	–	–
PtSn–OM	1	n.d.	n.d.	70.8	484.3	487.0	0.45
PtSn–BM	1	0.20	2.9	70.6	484.6	487.1	0.64



Scheme 1. Proposed images for PtSn-OM and PtSn-BM catalysts, based on characterization data and from Ref. [21].

Table 2
Catalytic results for (–)- α -pinene hydrogenation in liquid phase

Catalyst	TOF (s^{-1}) cyclohexene ^a	TOF (s^{-1})	% <i>trans</i> -pinane	% <i>cis</i> -pinane
Pt/SiO ₂	0.1660	0.11	15	86
PtSn-OM	0.0049	0.007	16	84
PtSn-BM	0.0123	0.002	18	82

Reaction conditions: $P = 1$ MPa of H₂; $T = 353$ K; $m_{cat} = 0.25$ g; solvent = *n*-decane; $m_{substrate} = 1.65$ mmol. Selectivities measured at 20% conversion.

^a Taken from Ref. [15].

percentage of ionic Sn (*ca.* 35%) also exists and it is probably located in the metal–support interface.

3.1. Hydrogenation of α -pinene

Table 2 shows the hydrogenation results of α -pinene with the three catalysts studied (also, the values of turnover frequencies for cyclohexene are indicated, taken from references [15]). As it can be observed, hydrogenation products are the two pinanes (*cis* and *trans*), and *cis*-pinane is the major product in all cases. These results are in agreement with previously published ones, referred to the hydrogenation of α -pinene over Pt/C, Pd/C and Ni catalysts, for which the yield of *cis*-pinane ranged from 48.5 to 98.5% depending on H₂ pressure and temperature applied [22]. Equal to what has been previously observed during cyclohexene hydrogenation [15], and as it was expected, there exists a very different activity when passing from Pt/SiO₂ to PtSn-BM and PtSn-OM catalysts. Thus, while the monometallic system reaches an almost total conversion in 100 min, the systems modified with Sn hardly achieve a conversion near 10% in this same time. The explanation of this reactivity decrease of the C=C bond can be interpreted as combined effects of blockage of the hydrogenation active sites and weakening of the Pt–olefin bond, as a consequence of the electronic effects of Sn on Pt.

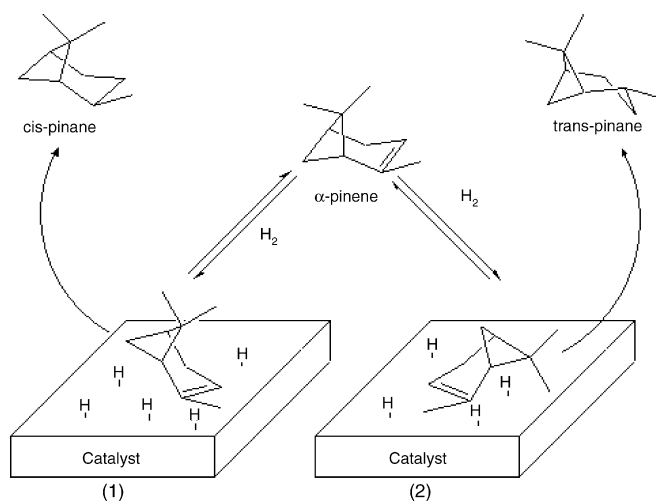
Scheme 2 explains the stereoselectivity of this reaction. In this case, it is necessary to analyze the geometric distribution of the different groups that compose the α -pinene molecule: it is evident that the two sp^2 -hybridized atoms forming the C=C bond in the α -pinene molecule generate a plane, and all substituents (–H, –CH₃ and the two C atoms) belong to this plane. The >CH_2 group and the most bulky one $\text{>C(CH}_3)_2$ are located in opposite sides of this plane. The π -orbital of the C=C bond is normal to this plane. The adsorption of the α -pinene molecule through its two faces produces two different π -complexes with superficial Pt atoms. Structure (1), in which the bulky $\text{>C(CH}_3)_2$ group is oriented in opposite direction to the metal surface, results to be the preferential geometrical arrangement because the steric

hindrance is lower. A maximum overlapping is obtained between π -orbitals of α -pinene and d orbitals of Pt. The formation of the superficial π -complex is accompanied by a shift of the –CH₃ group above the plane, so that both groups, $\text{>C(CH}_3)_2$ and –CH₃, remain in the same side of the plane. This structure predetermines the *cis*-pinane formation. The α -pinene molecule adsorption on the opposite side favors structure (2), that would pre-determine the *trans*-pinane formation.

3.2. Hydrogenation of verbanone, fenchone and camphor

These substrates were selected in order to evaluate the influence of the steric hindrance on the C=O group hydrogenation. Besides, in the case of fenchone and camphor, due to their different topographies, they usually present also different chemical properties [23].

Verbanone was hydrogenated with the three catalysts studied, Pt/SiO₂, PtSn-OM and PtSn-BM. This hydrogenation was stereoselective in all cases, and the *cis*-verbanol



Scheme 2. Hydrogenation of α -pinene. Schematic representation of the stereoselectivity of the reaction.

Table 3

Hydrogenation of *cis*-verbanone: initial reaction rate (r_i) and selectivities measured at 20% conversion

Catalyst	r_i ($\mu\text{mol s}^{-1} \text{g}_{\text{Pt}}^{-1}$)	TOF (s^{-1})	S% <i>cis</i> -verbanol	S% <i>trans</i> -verbanol
Pt/SiO ₂	2.8	5.46×10^{-4}	>99	–
PtSn-OM	6.9	1.35×10^{-3}	>99	–
PtSn-BM	6.7	1.31×10^{-3}	>99	–
NaBH ₄	–	–	96	4

Results for chemical reduction with NaBH₄ is also included. For experimental conditions, see the text.

was the major product. Table 3 shows the values of reaction rate and selectivity for verbanone hydrogenation. Reaction rates were very slow with the three catalysts, so, more than 300 min are necessary to reach 50% verbanone conversion. This could be explained as a function of the steric hindrance of the *gem*-dimethyl bridge of the molecule. Although still slow reactions, the Sn addition introduces a slight improvement in the activity of the catalysts, due to a more efficient polarization of the C=O group as a consequence of the Snⁿ⁺ presence that would act as a Lewis acid site.

Regarding the stereoselectivity of the C=O group hydrogenation of the verbanone, a selectivity over 99% towards *cis*-verbanol is observed. The explanation of this result is found when analyzing that the face that will result to be preferentially adsorbed is the one that leaves the >CH_2 and $\text{>C(CH}_3)_2$ groups far away from the catalyst surface, in a geometric arrangement that would be dominantly “pro-*cis*”.

During fenchone and camphor hydrogenation (Figs. 1 and 2, respectively), it was not possible to reach a complete conversion of substrates within a reaction time of more than 10 h. In the case of fenchone, the most restrained of the two terpenes, it only reached 20% conversion after 400 min under reaction using the Pt/SiO₂ catalyst. With Sn-modified catalysts, the conversion was hardly more than 2% in the same time, this behavior was surely caused by geometric and electronic modifications of the surface. The camphor hydrogenation

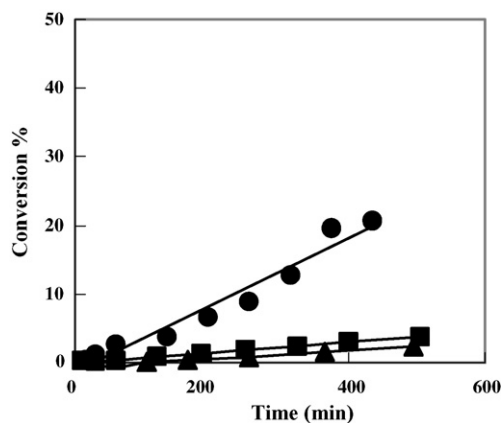


Fig. 1. Conversion of fenchone as a function of reaction time. Reaction conditions: $T = 353 \text{ K}$; $P = 1 \text{ MPa}$ of H_2 ; $m_{\text{cat}} = 0.25 \text{ g}$; solvent = *n*-decane; $m_{\text{substrate}} = 1.65 \text{ mmol}$. (●) Pt/SiO₂; (▲) PtSn-OM; (■) PtSn-BM.

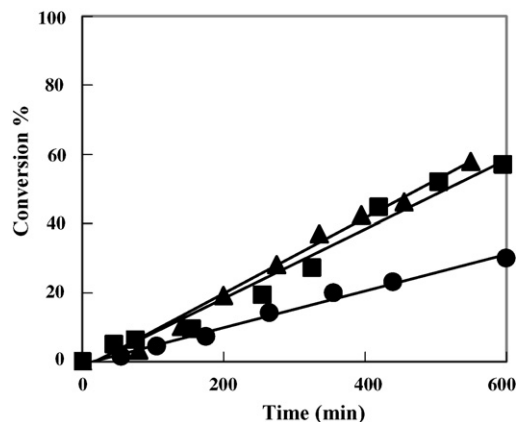
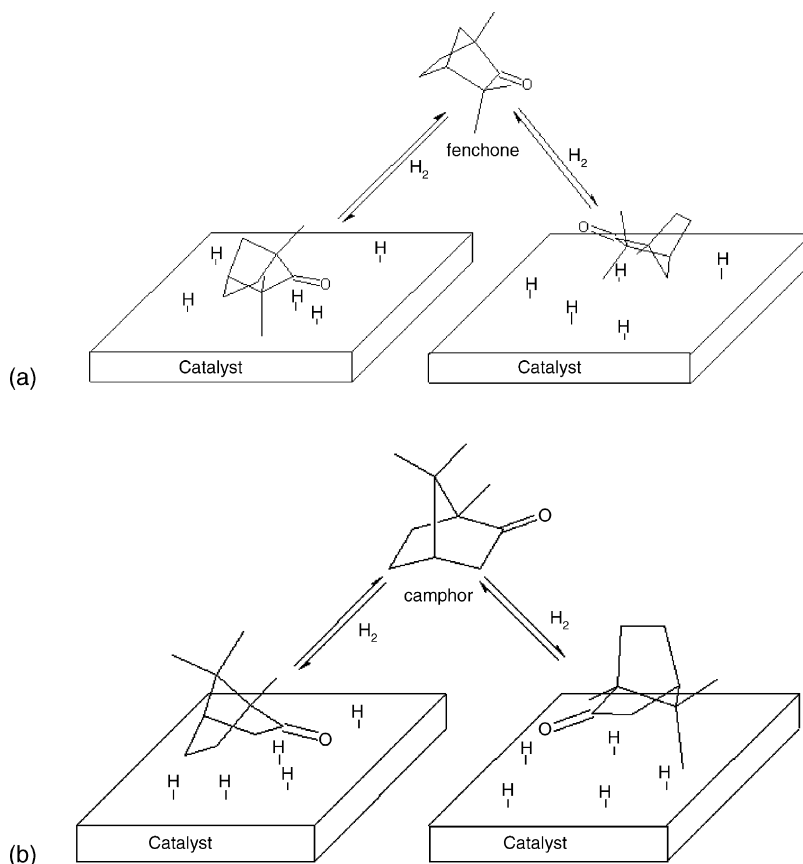


Fig. 2. Conversion of camphor as a function of reaction time. Reaction conditions: $T = 353 \text{ K}$; $P = 1 \text{ MPa}$ of H_2 ; $m_{\text{cat}} = 0.25 \text{ g}$; solvent = *n*-decane; $m_{\text{substrate}} = 1.65 \text{ mmol}$. (●) Pt/SiO₂; (▲) PtSn-OM; (■) PtSn-BM.

reached a conversion of about 20% in 360 min when Pt/SiO₂ was used as catalyst, showing a behavior similar to the one of fenchone. However, in this case, the use of catalysts modified with Sn had a positive effect on the activity (TOF (s^{-1}) = 0.0023 for Pt/SiO₂, 0.0047 for PtSn-OM and 0.0045 for PtSn-BM). The most efficient polarization of the C=O group of camphor in Sn-modified catalysts is surely responsible for the activity increase when passing from the monometallic to the bimetallic system.

The explanation of the dissimilar behavior between fenchone and camphor is found in the different steric hindrance presented by the two molecules. In fenchone, both diastereotopic faces of the C=O bond are sterically hindered: the hydrogenation reaction proceeds very slowly producing the preferential formation of *endo*-fenchyl alcohol, the thermodynamically more stable isomer (Scheme 3(a)). Due to the high steric hindrance of the molecule, the modification of the Pt/SiO₂ catalyst with Sn is not enough to improve the reaction rate, but it is effective in the case of camphor.

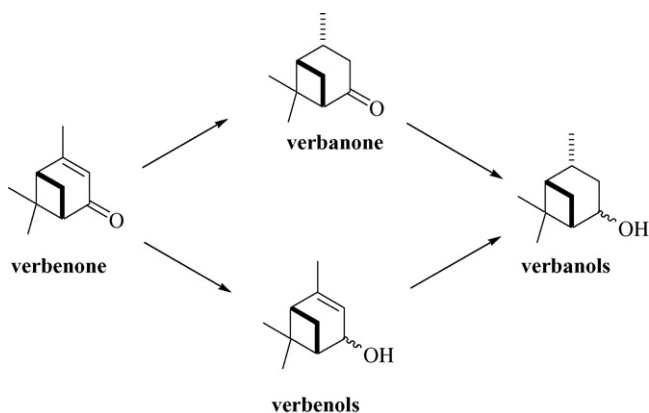
In the camphor hydrogenation, the high diastereoselectivity obtained is noticeable. The *exo*-isomer is preferentially formed with the three catalysts studied. This isomer is thermodynamically less stable although kinetically preferential [24]. However, when the monometallic catalyst is used, as the reaction is quite slower, a higher amount of *endo*-borneol is obtained (thermodynamically more stable) than when catalysts modified with Sn are used. The *exo*-borneol formation derives from coordination of the molecule with the catalyst surface through its “inferior” *endo*-face, thus allowing the adsorbed hydrogen to attack the C=O group from below. In Scheme 3(b), a possible way for camphor hydrogenation is represented. Geometric and electronic modifications and the steric hindrance that appear when tin modified catalysts are used, favoring even more the coordination of the camphor molecule through its less hindered face. The most important diastereoscopic difference between the two faces of C=O in the camphor compared with the fenchone allows to explain the higher hydrogenation rate observed in this last case.



Scheme 3. (a) Hydrogenation of fenchone. Schematic illustration of adsorption through both diastereotopic faces. (b) Hydrogenation of camphor. Schematic illustration of adsorption through both diastereotopic faces.

3.3. Hydrogenation of verbenone

Verbenone is an α,β -unsaturated ketone, whose hydrogenation can generate a series of products, as it is shown in Scheme 4. Thus, if the C=O group is selectively hydrogenated, unsaturated alcohols are obtained (*cis*- and *trans*-verbenol); when the double C=C bond is hydrogenated, the saturated ketone, verbanone, is obtained and the total hydrogenation of the molecule leads to the obtention of isomeric verbanols.



Scheme 4. Reaction pathway for verbenone hydrogenation.

The verbenone hydrogenation was tested with the three catalysts used, Pt/SiO₂, PtSn-OM and PtSn-BM. Fig. 3 shows the distribution of verbenone hydrogenation products when Pt/SiO₂ catalyst is employed. Results are in agreement with what is expected for the hydrogenation of a double C=C bond with metallic catalysts; this is the Pt/SiO₂ catalyst presents a high hydrogenation rate for a C=C bond, and so the total verbenone conversion to verbanone is obtained in less than 100 min. In a first stage, the hydrogenation of the C=C bond occurs to give *cis*-verbanone. Once the substrate has reacted almost

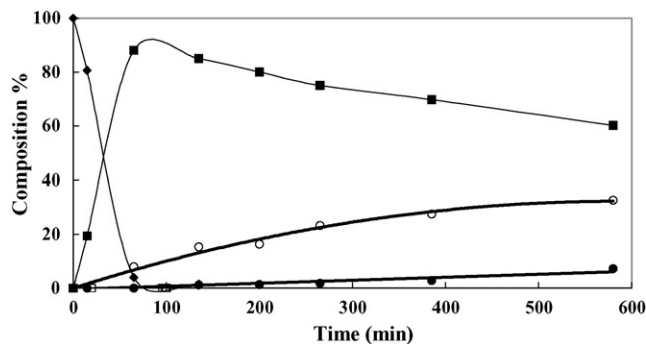


Fig. 3. Hydrogenation of verbenone. Concentration profiles along the reaction on Pt/SiO₂. (◆) verbenone; (■) *cis*-verbanone; (○) *cis*-verbanol; (●) *trans*-verbanol. Reaction conditions: $T = 353$ K; $P = 1$ MPa of H₂; $m_{\text{cat}} = 0.25$ g; solvent = *n*-decane; $m_{\text{substrate}} = 1.65$ mmol.

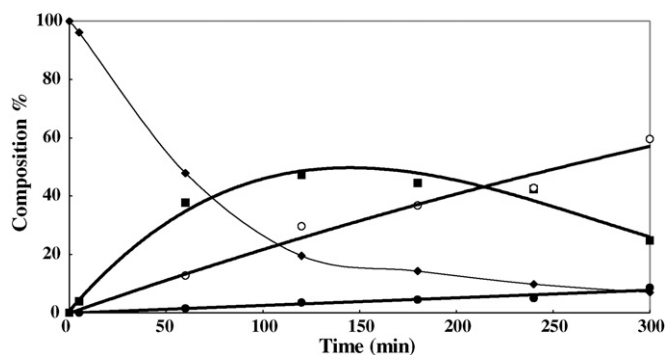


Fig. 4. Hydrogenation of verbenone. Concentration profiles along the reaction on PtSn-BM. (◆) verbenone; (■) *cis*-verbanone; (○) *cis*-verbanol; (●) *trans*-verbanol. Reaction conditions: $T = 353$ K; $P = 1$ MPa of H_2 ; $m_{cat} = 0.25$ g; solvent = *n*-decane; $m_{substrate} = 1.65$ mmol.

completely, the subsequent *cis*-verbanone hydrogenation proceeds very slowly with verbanol production, particularly the *cis*-isomer. Then, after 400 min, the following mixture of products is obtained: 71% *cis*-verbanone, 31% *cis*-verbanol and 4.5% *trans*-verbanol.

With respect to the stereoselectivity of the first reaction stage, similar to the case of the hydrogenation of the C=C bond of α -pinene, the *cis*-isomer formation of verbanone is favored because it comes from an adsorption mode corresponding to a less hindered geometrical arrangement of the molecule (with bulky groups in the side opposite to the adsorption plane). The subsequent hydrogenation of the C=O bond generates large amounts of *cis*-verbanol, as it was observed in the verbanone hydrogenation.

It is interesting to remark that catalysts modified with Sn lead to the obtention of a main product different from the one achieved with the monometallic catalyst or with $NaBH_4$. Figs. 4 and 5 present hydrogenation results of verbenone using Sn-modified catalysts. The reaction rate of verbenone with both PtSn-BM and PtSn-OM is lower than the one with the monometallic catalyst (r_i ($\mu\text{mol s}^{-1} \text{g}_{Pt}^{-1}$): 193 (PtSn-BM); 149 (PtSn-OM) and 281 (Pt/SiO₂)). The same tendency is followed as in the case of the hydrogenation of the double bond of α -pinene, but differences among the catalysts are not so

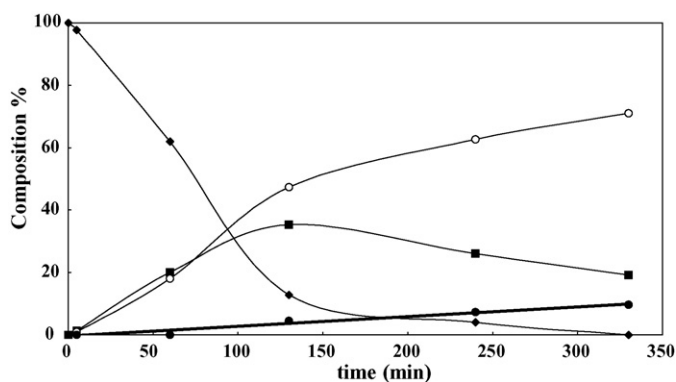


Fig. 5. Hydrogenation of verbenone. Concentration profiles along the reaction on PtSn-OM. (◆) verbenone; (■) *cis*-verbanone; (○) *cis*-verbanol; (●) *trans*-verbanol. Reaction conditions: $T = 353$ K; $P = 1$ MPa of H_2 ; $m_{cat} = 0.25$ g; solvent = *n*-decane; $m_{substrate} = 1.65$ mmol.

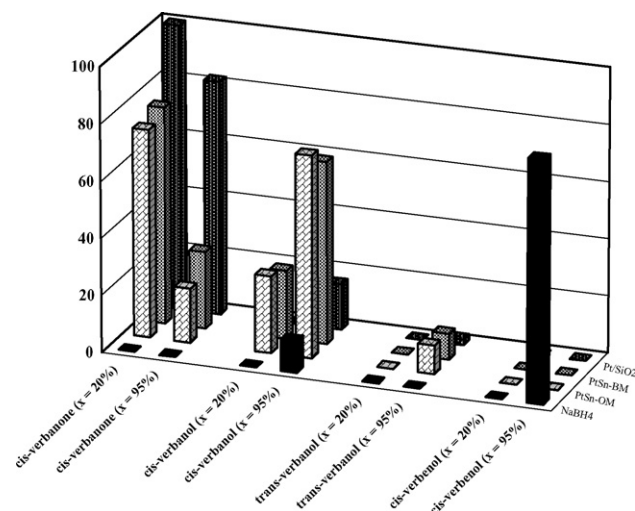


Fig. 6. Selectivities of verbenone hydrogenation products at two levels of conversion (20 and 95%) for the three catalytic systems employed (Pt/SiO₂, PtSn-BM and PtSn-OM) and for the chemical reduction with $NaBH_4$. For reaction details, see Section 2.

marked. The verbenone behavior is analogous to the one observed in the case of pulegone hydrogenation with bi- and organobimetallic catalysts, and it is opposite to what occurs with α,β -unsaturated aldehydes [15,25]. Thus, in the case of verbenone, the C=C bond is preferentially hydrogenated and the product of the selective hydrogenation of the C=O bond, *cis*-verbanol, was not observed. With both tin modified catalysts, the product formed in first place is the *cis*-verbanone, as in the case of Pt/SiO₂ catalyst. An interesting aspect to point out is that the catalysts modified with Sn are able to carry out the two successive hydrogenation stages with a good selectivity to verbanol. Another point is that the second hydrogenation stage (from verbanone to verbanol) is slower than the same transformation when the starting substrate is pure verbanone. This result could be assigned to a higher poisoning of the catalyst surface in presence of verbenone due to formation of some oligomers, equal to the case of other unsaturated carbonyl compounds [26].

In the bar diagram of Fig. 6, results of verbenone reduction with the three catalysts studied are summarized, the result of its reduction with $NaBH_4$ is also presented. A large difference exists between the behavior of verbenone reduction with $NaBH_4$ and with the different heterogeneous catalysts studied: with $NaBH_4$, the major product resulted to be the *cis*-verbanol, with a small contribution of *cis*-verbanone, the product of complete reduction. This compound is very reactive and produces a quick and specific reduction of the C=O group generating the corresponding unsaturated alcohol. The Pt/SiO₂ catalyst allows to obtain *cis*-verbanone with high yield and catalysts modified with Sn generate *cis*-verbanol as major product.

4. Conclusions

From the obtained results, it is evident that the activity and the chemo- and stereoselectivity in the hydrogenation of C=C

and C=O groups present in the terpenes analyzed can be controlled by modifying the classical Pt/SiO₂ catalysts with SnBu₄.

In the hydrogenation of α -pinene, the monometallic system reaches an almost total conversion to *cis*-pinane in 100 min, while the systems modified with Sn hardly achieve a conversion near 10% in this same time. This fact can be explained by combined electronic and geometrical effects.

For sterically hindered terpenones, the topography of the molecule is of fundamental importance. Thus, while in the fenchone the presence of the *gem*-dimethyl group neighbor to the C=O group restricts the approach to the catalyst surface, a preferential face exists in the camphor that leads to the production of *exo*-borneol. In fenchone, both diastereotopic faces of the C=O bond are sterically hindered: the hydrogenation reaction proceeds very slowly producing the preferential formation of *endo*-fenchyl alcohol, the thermodynamically more stable isomer. Due to the high steric hindrance of the molecule, the modification of the Pt/SiO₂ catalyst with Sn is not enough to improve the reaction rate, but it is effective in the case of camphor.

In verbenone hydrogenation, the Pt/SiO₂ catalyst allows to obtain *cis*-verbanone with high yield and catalysts modified with Sn lead to the obtention of a different principal product (*cis*-verbanol) than the one obtained by chemical reduction with NaBH₄ (*cis*-verbenol). The formation of *cis*-verbanone is favored because it comes from an adsorption mode corresponding to a less hindered geometrical arrangement of the molecule (with bulky groups in the side opposite to the adsorption plane). The subsequent hydrogenation of the C=O bond keeps the stereoselectivity to *cis*-verbanol, as it was observed in the verbanone hydrogenation.

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