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Study of the racemic and enantioselective hydrogenation of acetophenone and 3,4-dimethoxyacetophenone using platinum-based organotin catalysts

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Abstract

In this work, some results of the racemic and enantioselective hydrogenation of acetophenone and 3,4-dimethoxyacetophenone are presented. The employed catalysts were platinum-based modified with organotin precursors either chiral (Men_3Sn-$SnMen_3$) or achiral ($SnBu_4$), and they were obtained via surface organometallic chemistry on metals (SOMC/M) techniques. The presence of organotin fragments on the catalyst surface inhibits the aromatic ring hydrogenation, leading to the hydrogenation of both acetophenone and 3,4-dimethoxyacetophenone to the corresponding alcohol with selectivity higher than 99%. With both substrates, a rate acceleration when changing from the achiral catalyst PtSn-OM to the chiral one, PtSn-OM* was observed. The presence of menthyl groups may be responsible for the rate acceleration in the key step of enantiodifferentiation. In the 3,4-dimethoxyacetophenone hydrogenation, 39% enantiomeric excess was obtained, with a selectivity of nearly 100%.
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1. Introduction

The control of the selectivity in the hydrogenation of molecules containing C=C and C=O groups is a widely studied topic [1–4]. On the other hand, a related subject as it is the competitive hydrogenation of a C=O group and an aromatic ring present in the same molecule has been less discussed in the literature up to the moment. The importance of the subject derives from the use of the reduction of aromatic ketones in order to obtain the corresponding alcohols. These compounds are extensively used in the production of medicines and fine chemical products [[5] and

references therein]. Many of these products are required as monoenantiomeric drugs or at least with high optical purity [5,6]. For this reason, during these last years, important efforts are being done in the research and development of heterogeneous catalysts with enantioselective hydrogenation capacity. For example, metal–ligand complexes can be immobilized by covalent or coordinative linkage or electrostatic attraction via functionalized ligands or by adsorption on porous supports [[7] and references therein]. However, up to the moment, high enantioselectivities have been obtained only for a reduced number of heterogeneous catalytic systems: Raney Ni catalysts modified with tartrate/NaBr [8] are virtually 100% specific to hydrogenate β-ketoesters and systems based on Pt modified with alkaloids of the cinchona family present high selectivity in the

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hydrogenation of α-ketoesters [9]. These kind of systems are successfully employed nowadays for the hydrogenation of certain carbonyl compounds [6,10–14]. For this reason, new and innovating ways of obtaining heterogeneous asymmetric catalysts are appearing from day to day [15,16].

The method selected to obtain chiral heterogeneous catalysts presented in this work, was to deposit a chiral organic fragment on the surface of a supported metallic catalyst. This is based on the previous experience of our work group in developing organometallic heterogeneous catalysts by using Surface Organometallic Chemistry on Metals techniques (SOMC/M) [17–21]. These techniques provide the possibility of adding selectively a promoter metal on another supported metal (usually a transition one) and stabilizing organic fragments on the bimetallic phase. The addition of organic fragments of chiral nature allows us to obtain stable supported organometallic phases able to preserve the hydrogenating properties of the base catalyst, besides orienting the reaction enantioselectivity [16].

Catalysts here presented are tested in the hydrogenation of acetophenone and 3,4-dimethoxyacetophenone. These substrates result very interesting to be analyzed from the point of view of the relation between their molecular structure and their reactivity, taking into account the competitive hydrogenation of the carbonyl group and the aromatic ring. With the aim to understand the different functions of the chiral organometallic catalyst (hydrogenating capacity and enantiodifferentiation capacity) in the enantioselective hydrogenation of substrates, their racemic hydrogenation was also studied, using an achiral organometallic catalyst. Catalysts studied were based on Pt/SiO$_2$ modified by chiral (Men$_3$Sn-SnMen$_3$) and achiral organometallic precursors (SnBu$_4$).

2. Experimental

2.1. Synthesis of the precursor hexa($-$)-menthylditin (Men$_3$Sn-SnMen$_3$)

The reaction was carried out following the Podestá and Radivoy technique [22]. A volume of 150 mL of a solution 1.58 M (0.240 mol) of ($-$)-menthylmagnesium chloride in dry THF, was added drop by drop to a solution of 10.3 g (0.040 mol) of SnCl$_4$ in 48 mL of dry C$_6$H$_6$, in an ice bath. Once the addition step was finished, the reaction mixture was heated under reflux for 60 h and then it was cooled down to room temperature under stirring. A 10% HCl solution (25 mL) was added and diluted with distilled water (25 mL). After the adition of ethyl ether (200 mL), the organic phase was separated and dried on anhydrous MgSO$_4$. The solvent was distilled under reduced pressure and the product was recrystallized in ethanol, yielding 12.9 g (0.012 mol, 59.8%) of hexa($-$)-menthylditin (Men$_3$Sn-SnMen$_3$; Men: menthyl); m.p. 503 K (dec.), $[\alpha]^{20}_D = -21.4°$ (0.99; dry benzene). The obtained compound was characterized by NMR of ^{1}H, ^{13}C

and ^{119}Sn in a Bruker ARX 300 equipment, using CDCl$_3$ with tetramethylsilane as the standard.

2.2. Catalysts preparation

The detailed procedure followed to prepare Pt/SiO$_2$ monometallic catalyst has been previously published [21]. The modification of monometallic catalysts by tin addition was carried out by using surface organometallic chemistry on metals (SOMC/M) techniques. After the reduction stage, a definite quantity of the monometallic catalyst (0.25 g) is put to react in H$_2$ atmosphere with SnBu$_4$ dissolved in n-decane at 393 K. Once the reaction is finished, the catalyst is washed with several portions of n-heptane in Ar atmosphere. This catalyst, that has a molar ratio Sn/Pt = 0.8, is denominated PtSn-OM and corresponds to a solid containing butyl groups anchored on the metallic surface. The preparation of the chiral organometallic catalyst was performed by following an analogous procedure, but using a solution of the chiral organotin compound hexa($-$)-menthyldtin in n-heptane. The Sn/Pt ratio used was also 0.8. This catalyst is denominated PtSn-OM*. Before loading the catalysts into the reactor for the hydrogenation tests, n-heptane was changed for isopropylalcohol (the reaction solvent). Special care was taken not to expose the catalyst to atmosphere.

2.3. Catalysts characterization

The variation in the concentration of the Sn compound and the amount of hydrocarbons removed during the preparation of PtSn-OM catalyst, were analyzed using a gas chromatograph Varian 3400 CX (column 10% OV-101, FID) and a GC/MS Shimadzu QP 5050A (capillary column SPB-%^{TM} Supelco). The Sn content was determined by a colorimetric technique after complexing the tin with phenylfluorone. After dissolving the samples with HCl, 100 mg of each one were weighed, 40 mL of HCl 1:1 were added and then the mixture was heated for 12 h in an Erlenmeyer flask provided with a Bunsen valve. The solution was filtered by suction, the solid was washed and the filtrate was diluted to 250 mL with acidulated water. H$_2$O$_2$ 3%, CH$_3$COOH/CH$_3$COONa buffer and solution of sodium dodecylsulfate 1% were added. Then, under stirring, phenylfluorone in methanol was added to each solution, waiting 15 min for color development. The resulting solutions were diluted to 50 mL with HCl 1:9. The absorbance of the solutions was determined in a GBC Cintra 40 UV–Vis spectrometer, at 530 nm. The Pt content was determined by atomic absorption.

H$_2$ chemisorption was measured in a static volumetric apparatus at ambient temperature for Pt/SiO$_2$ sample employing the double isotherm method [21]. The size distribution of metallic particles for Pt/SiO$_2$ catalyst 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 analysis was obtained with an ESCA 750 Shimadzu spectrometer equipped with a hemispherical electron analyser 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. Organometallic samples were dried and Pt/SiO$_2$ sample was 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 substraction of the S-shaped background and fitting the experimental peak to a Lorentzian/Gaussian mix of variable proportion.

2.4. Hydrogenation reactions

Both the racemic and the enantioselective hydrogenations of acetophenone and 3,4-dimethoxyacetophenone were carried out in a stirred autoclave type reactor at a pressure of H$_2$ of 1 MPa and a temperature of 353 K, using 0.25 g catalyst, and isopropyl alcohol as solvent. In each test, a ketone amount corresponding to 4.3 mmol was used. The experimental conditions for the catalytic tests were chosen so that the reaction rate was not influenced by mass transfer. Reaction rates were measured at short reaction times and conversion values under 10%. 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 FID. The identification of the diverse reaction products, was accomplished by GC/MS in a Shimadzu QP5050 equipment. The enantiomeric excess (e_e) was calculated according to the following expression: $e_e\% = 100(S - R)/(S + R)$, taking into account data obtained with a CP-Chirasil-Dex CB column (25 m length and 0.25 mm i.d.) in a GC Varian 3400 gas chromatograph.

3. Results and discussion

The key step in the preparation of PtS-OM* catalyst is the obtention of the chiral organotin compound used as precursor, that can be described by Eq. (1):
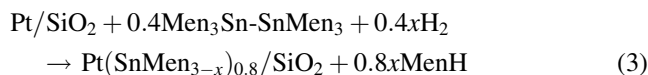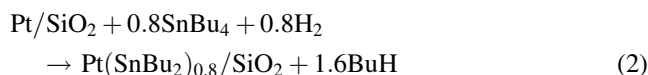
$$SnCl_4 + (-) - MenMgCl \xrightarrow{benzene} (-) - Men_3Sn - Sn(-) - Men_3 \quad (1)$$
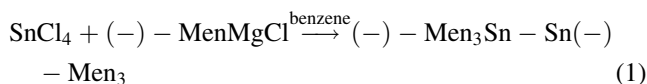
The ^{1}H, ^{13}C and ^{119}Sn NMR characteristics of the synthesized compound are:

- ^{1}H RMN^a: 0,73 (d, 18H); 0,79 (d, 18H); 0,84 (d, 18H); 1,07–2,17 (m, 60H).
- ^{13}C RMN^b: 17,32; 22,10; 22,42; 27,63 (46,3); 34,43 (11,8); 35,70; 36,54 (63,7); 39,62 (196,4); 45,50; 46,30 (19,0).
- ^{119}Sn RMN^c: 18 ppm

- ^{a}In CDCl$_3$; chemical shifts, δ, in ppm with respect to TMS; multiplicity, n°H, coupling constants ^nJ(Sn,H) in Hz, between parenthesis.
- ^{b}In CDCl$_3$; chemical shifts, δ, in ppm with respect to TMS; coupling constants ^nJ(Sn,C) in Hz, between parentheses.
- ^{c}In CDCl$_3$; chemical shifts, δ, in ppm with respect to (CH$_3$)$_4$Sn.

These results indicate that the compound was obtained optically pure, without epimerization in the carbon atom of the menthyl group bonded to the tin atom.

The preparation of the Pt/SiO$_2$ employed as base catalyst by means of ionic exchange allowed to obtain a catalytic phase with high dispersion (H/Pt = 0.64, measured by H$_2$ chemisorption). Results obtained by TEM showed a rather uniform distribution of particles size, centered around 2.5 nm. These characteristics of surface homogeneity are essential to assure a correct preparation of organometallic catalysts through SOMC/M techniques. The reaction between the reduced monometallic catalyst and each one of the two organotin compounds used can be described by the following equations:

$$Pt/SiO_2 + 0.8SnBu_4 + 0.8H_2 \\ \rightarrow Pt(SnBu_2)_{0.8}/SiO_2 + 1.6BuH \quad (2)$$

$$Pt/SiO_2 + 0.4Men_3Sn\text{-}SnMen_3 + 0.4xH_2 \\ \rightarrow Pt(SnMen_{3-x})_{0.8}/SiO_2 + 0.8xMenH \quad (3)$$

Eq. (2) represents the obtention of the achiral organometallic catalyst (PtSn-OM) and Eq. (3) the one corresponding to the chiral catalyst (PtSn-OM*). With respect to this last catalyst, it should be noted that, up to the moment, we have performed no further characterization of the phase, and so the true nature of the superficial complex is not yet really known. Nevertheless, in the light of the results obtained, one or more menthyl groups surely remain bonded to the tin, giving to the phase its enantiodifferenciating capacity. In the PtSn-OM catalyst, according to XPS measurements, Pt is completely reduced and tin is found as Sn(0) and Sn(II,IV) in similar proportions. Blank experiments were conducted in which both tin precursors were contacted with the silica, and no detectable quantities of tin were found on the support, under the experimental conditions here employed.

3.1. Racemic hydrogenation of acetophenone and 3,4-dimethoxyacetophenone

The main products of acetophenone hydrogenation are shown in Scheme 1. If the C=O bond is hydrogenated, 1-phenylethanol (1) is obtained, a product of interest in pharmaceutic and perfume industry. On the other hand, the hydrogenation of the aromatic ring leads to the achievement of cyclohexylmethylketone (2). Finally, the subsequent hydrogenation of 1 or 2 leads to 1-cyclohexylethanol (3), a product used in the manufacture of certain polymers. Fig. 1a
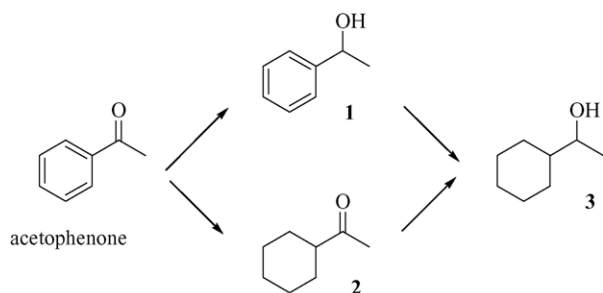
Scheme 1. Reaction scheme for acetophenone hydrogenation.

and b depict the variation of the reaction mixture composition as a function of time for Pt/SiO$_2$ and for PtSn-OM catalysts. For the Pt/SiO$_2$ catalyst (Fig. 1a), at the beginning of the reaction, **1** and **2** are produced in similar proportions. In the course of the reaction, **1** and **2** hydrogenation also occurs to render the completely hydrogenated product **3** and also appear ethylbenzene and ethylcyclohexane. The formation of ethylbenzene and ethylcyclohexane could be explained by hydrogenolysis
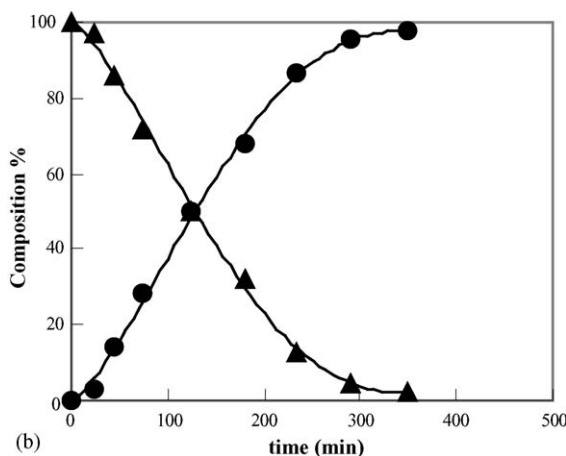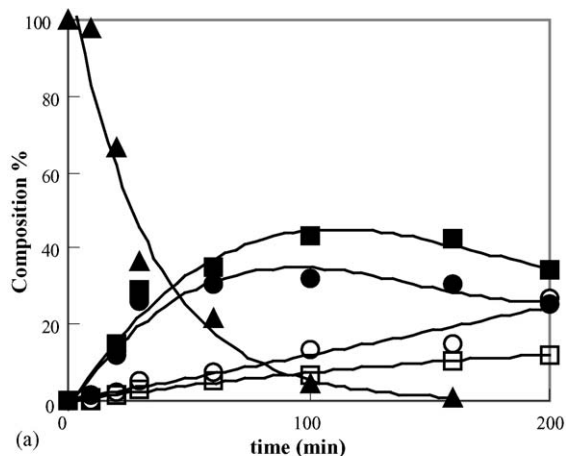

Fig. 1. Product distribution (mol%) during the course of acetophenone hydrogenation (353 K, 1 MPa H$_2$, 0.25 g catalyst): (a) Pt/SiO$_2$ catalyst; (b) PtSn-OM catalyst. ((▲) Acetophenone, (●) 1, (■) 2, (○) 3, (□) ethylbenzene and ethylcyclohexane).

Table 1
Racemic hydrogenation of acetophenone

Catalyst	Sn/Pt	r_i[a]	1 (%)	2 (%)	3 (%)	Others (%)[b]
Pt/SiO$_2$	0	425	31	43	15	11
PtSn-OM	0.8	102	>99	–	–	–

Initial reaction rate (r_i) (μmol g$_{Pts}^{-1}$ s^{-1}). Selectivity to product at 100% of conversion.

[a] Estimated between conversion 0 and 10%.

[b] Ethylbenzene and ethylcyclohexane.

of the C–O bond of the intermediate alcohols or, as it has been proposed in the literature, by the initial C=O hydrogenation followed by dehydration and addition of hydrogen to the newly formed C=C bond [23]. Total conversion of acetophenone is reached at 160 min reaction and selectivity measured at this point corresponds to a complex mixture of products that makes the reaction scarcely useful for the obtention of product **1** (Table 1).

The presence of tin changes considerably the catalytic performance for the acetophenone hydrogenation, especially in terms of activity and selectivity: for PtSn-OM catalyst, the selectivity to 1-phenylethanol (**1**) is notably increased, exceeding 99% and besides, the most interesting result is the fact that no subsequent hydrogenation to **3** is observed (Fig. 1b and Table 1). Total conversion of acetophenone is reached at 350 min reaction time.

These differences in the performance of Pt/SiO$_2$ and PtSn-OM go in the same direction of previously published results about how the modification of a platinum surface causes a decrease in the hydrogenation rate of acetophenone [24]. As it is shown in Scheme 2, on Pt/SiO$_2$ catalyst, the acetophenone molecule can be coordinated to the surface according to two modes, one way is of the η^1(O) type, in which the molecule is coordinated to the surface through the oxygen of the C=O group. The aromatic ring remains parallel to the surface and consequently it is susceptible to be hydrogenated. The other adsorption mode is of the type η^2(C,O), in which the carbonyl group is coordinated through its π electron system. The aromatic ring remains inclined with respect to the surface. This last configuration is the one supposed to originate the ethylbenzene appearance according to what was published in bibliography [25]. In the PtSn-OM catalyst, the aromatic ring hydrogenation is strongly
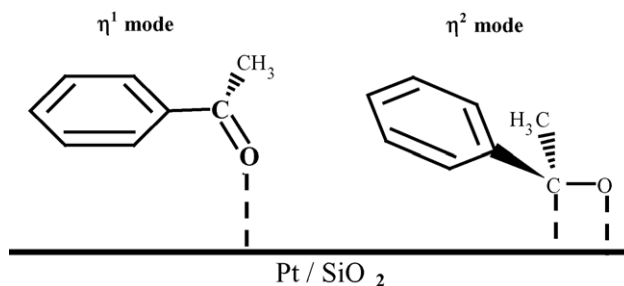
Scheme 2. Adsorption modes for acetophenone molecule (taken from reference [10]).
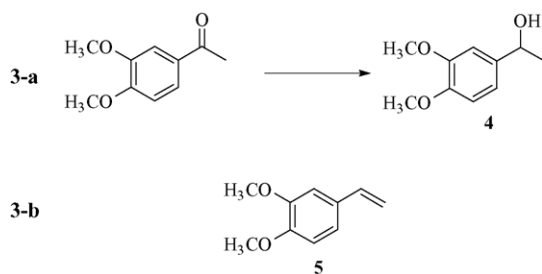
Scheme 3. (a) Hydrogenation of 3,4-dimethoxyacetophenone. (b): 3,4-Dimethoxypropene, dehydration product of 3,4-dimethoxybenzylalcohol.

inhibited perhaps by a dilution effect of Pt atoms, besides the electronic effects produced by the presence of ionic tin, as it is determined by XPS [2]. Both effects would favor the acetophenone molecule interaction in this catalyst through the oxygen atom of the C=O group, and not via the aromatic ring, facilitating in this way the formation of compound 1. The existence of an additional steric effect due to the presence of SnBu$_x$ fragments on the surface should not be discarded. All these facts lead to a selectivity toward compound 1 of practically 100%.

Catalytic hydrogenation of substituted acetophenones is a useful reaction to obtain the corresponding alcohols; for example, *p*-isobutyl-acetophenone hydrogenation leads to 1-(*p*-isobutyl phenyl) ethanol in a key step to synthesize Ibuprofen®, a non-steroidal anti-inflammatory drug [26]. The 3,4-dimethoxyacetophenone hydrogenation was analyzed as an example of a ketone substituted in the aromatic ring used as intermediate in the synthesis of pharmaceutical products [27]. It would be expected that the 3,4-dimethoxyacetophenone hydrogenation had a similar behavior to the one of the acetophenone, giving a variety of products as consequence of the hydrogenation of the carbonyl group and the aromatic ring. However, with both catalysts studied a unique reduction product was obtained, the corresponding benzyl alcohol 4 (3,4-dimethoxyphenylethanol) (Scheme 3a). The selectivity to the benzyl alcohol may be discussed in terms of the competitive adsorption of the aromatic ring and the C=O bond on the metallic surface. This selectivity can be improved by decreasing the binding energy of the aromatic ring as a result of an increase of the repulsive electronic interaction with the metallic catalytic surface, which may occur due to the presence of electron-releasing substituents on the aromatic ring, such as –OCH$_3$ group. In this way, it would be possible to explain why with a catalysts such as Pt/SiO$_2$, the only hydrogenation product of 3,4-dimethoxyacetophenone is the benzyl alcohol 4. In the case of PtSn-OM catalyst, besides this fact, the already mentioned effects of Pt atoms dilution and the electronic modifications introduced by ionic tin, have to be considered.

Results presented in Fig. 2 (conversion versus time) and Table 2 indicate that for both studied catalysts, the reaction rate was lower than the corresponding values observed in the hydrogenation of acetophenone. This fact has been explained in terms of the mesomeric effect due to the –OCH$_3$ in
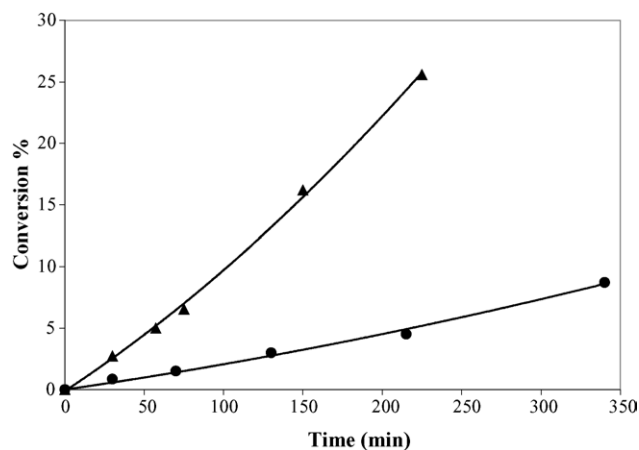

Fig. 2. Hydrogenation of 3,4-dimethoxyacetophenone (353 K, 1 MPa H$_2$, 0.25 g catalyst). Conversion as a function of time for (●) Pt/SiO$_2$ and (▲) PtSn-OM, catalysts.

p-position, which causes a higher repulsion between the C=O group and the platinum surface [28].

Finally, product 5 (Scheme 3-b) that appears in the chromatographic analysis, is a dehydration product, whose formation is most likely favored by the temperature of the GC oven and the stability of the benzyl carbocation by the presence of –OCH$_3$. The existence of the alcohol, as the single product of the hydrogenation reaction, was corroborated by ^{1}H NMR in the final reaction mixture.

3.2. Enantioselective hydrogenation of acetophenone and 3,4-dimethoxyacetophenone

The chiral catalyst prepared employing Men$_3$Sn-SnMen$_3$ as precursor compound (PtSn-OM*), was studied in the enantioselective hydrogenation of acetophenone and 3,4-dimethoxyacetophenone. Conversion results as a function of time for both substrates are presented in Fig. 3. When studying enantioselective hydrogenation reactions, a commonly observed phenomenon is the rate acceleration with respect to the racemic hydrogenation using the monometallic catalyst Pt/SiO$_2$. This phenomenon was effectively observed during the 3,4-dimethoxyacetophenone hydrogenation ($r_i = 154$ μmol s^{-1}g$_{Pts}^{-1}$ for PtSn-OM* versus 7 μmol s^{-1}g$_{Pts}^{-1}$ for Pt/SiO$_2$), as well as in the acetophenone hydrogenation, considering the hydrogenation rate of the C=O group to the corresponding alcohol for both catalysts ($r_i = 430$ μmol s^{-1}g$_{Pts}^{-1}$ for PtSn-OM* versus r_1

Table 2
Racemic hydrogenation of 3,4-dimethoxyacetophenone

Catalyst	r_i[a]	3,4-Dimethoxyphenylethanol (%)
Pt/SiO$_2$	7	>99
PtSn-OM	46	>99

Initial reaction rate (r_i) (μmol g$_{Pts}^{-1}$ s^{-1}). Selectivity to product at 20% of conversion.
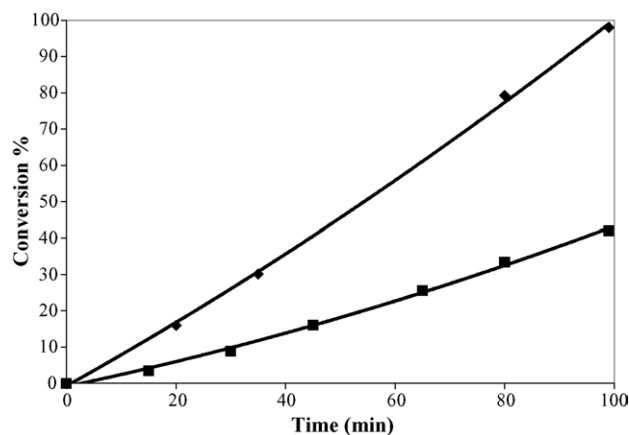
[a] Estimated between conversion 0 and 10%.

Fig. 3. Enantioselective hydrogenation of acetophenone and 3,4-dimethoxyacetophenone (353 K, 1 MPa H$_2$, 0.25 g catalyst). Conversion as a function of time for PtSn-OM* catalyst. (◆) Acetophenone, (■)3,4-dimethoxyacetophenone.

Fig. 4. Conversion, selectivity and enantiomeric excess for the hydrogenation of acetophenone and 3,4-dimethoxyacetophenone (353 K, 1 MPa H$_2$, 0.25 g catalyst).

(formation rate of **1**) = 165 μmol s^{-1}g$_{Pts}$$^{-1}$ for Pt/SiO$_2$). The largest differences in the hydrogenation rate between modified and unmodified catalysts are observed for 3,4-dimethoxyacetophenone, the substrate having the lower reactivity. These results were also found by Vargas et al., when studying the enantioselective hydrogenation of α-substituted ketones [29]. These results are in agreement with the ones found in the enantioselective hydrogenation of ethyl pyruvate employing a PtSn catalyst modified with cinchonidine [30].

Another important fact that appears when comparing both substrates is the rate difference observed while using the achiral organometallic catalyst PtSn-OM and the chiral organometallic catalyst, PtSn-OM*. In both cases an increase in the hydrogenation rate is produced for PtSn-OM* catalyst. The presence of chiral menthyl groups on the surface must be the responsible for establishing, which we can denominate "interaction geometry", causing the acceleration of the reaction in the key step of enantiodifferentiation.

Fig. 4 shows that the 3,4-dimethoxyacetophenone hydrogenation is produced with an e_e% higher than the one reached for the acetophenone. This constitutes an evidence contrary to what is obtained in the classic enanatioselective catalytic systems based on Pt modified with cinchonidine, for which the presence of an activating group (electron acceptor) in an α-position is necessary to obtain important values of enantioselectivity [24]. Evidently, the "interaction geometry" with substrates produced by the presence of menthyltin fragments results decisive for the key step of enantiodifferentiation. As it is observed in Fig. 4, an additional advantage of the catalytic systems here proposed is that the hydrogenation of both studied substrates is produced with a selectivity of practically 100% toward the corresponding benzyl alcohol, different from results of the literature, in which the yields do not overcome the 10% [24]. Finally, another important advantage of these types of catalytic systems here presented, is their stability. As it has been previously published, recycling of the
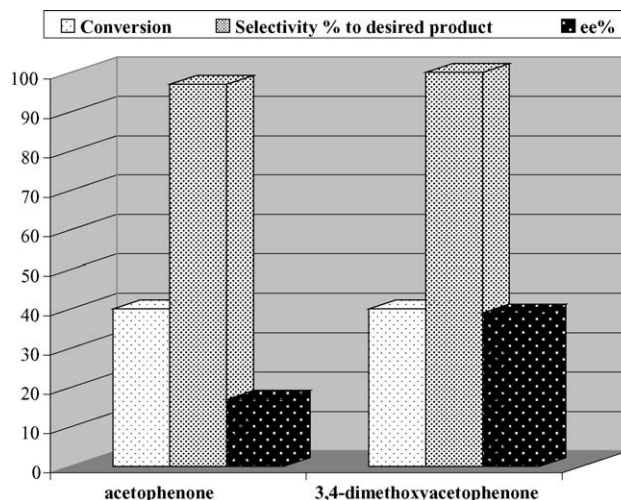
used catalyst is possible, without any loss in the selectivity or in the e_e% value obtained [16].

4. Conclusions

The principal conclusions of this work can be summarized as follows:

- In the hydrogenation of acetophenone and 3,4-dimethoxyacetophenone with PtSn-OM and PtSn-OM* catalysts prepared via SOMC/M, it was demonstrated that it is possible to obtain selectivities higher than 99% toward the corresponding benzyl alcohols.
- The presence of –OCH$_3$ groups electronically enriches the molecule of 3,4-dimethoxyacetophenone. This fact makes its hydrogenation rate being lower than the one of acetophenone, in the racemic as well as in the enantioselective hydrogenation.
- With both substrates studied, a rate increase was observed when passing from the racemic to the enantioselective hydrogenation. The effect is more noticeable for 3,4-dimethoxyacetophenone, the substrate having the lower reactivity. In the enantioselective hydrogenation, the presence of chiral menthyl groups probably causes the additional reaction rate acceleration in the key step of enantiodifferentiation.
- Important e_e% values were obtained by using PtSn-OM* catalyst. It is worth noting that this enantioselectivity is obtained with a selectivity of practically 100% toward the corresponding benzyl alcohol.

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