

## ENANTIOSELECTIVE HYDROGENATION OF ETHYL PYRUVATE WITH CINCHONIDINE MODIFIED Pt/SiO<sub>2</sub> AND PtSn/SiO<sub>2</sub> CATALYSTS

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Received December 11, 2002. In final form April 22, 2003

### Abstract

*The enantioselective hydrogenation of ethyl pyruvate on Pt/SiO<sub>2</sub> catalysts modified with a chiral compound, cinchonidine, and promoted with tin was studied in this work. The enantioselectivity of the nonpromoted Pt/SiO<sub>2</sub> catalysts depends strongly on the particle size; when the particle size is larger, the enantiomeric excess obtained is higher. The addition of small tin amounts (Sn/Pt= 0.01) produces a slight increase in the initial hydrogenation rate, and at the same time, a relative small change in the ee% value, but larger tin amounts generate a decrease in the initial hydrogenation rate together with a marked diminution of the ee value.*

### Resumen

*En este trabajo se estudió la hidrogenación enantioselectiva de piruvato de etilo empleando catalizadores de Pt/SiO<sub>2</sub> modificados con un compuesto quiral, la cinchonidina, y promovidos con estaño. La enantioselectividad de los catalizadores de Pt/SiO<sub>2</sub> no promovidos, depende fuertemente del tamaño de las partículas metálicas: a mayor tamaño de las partículas, más alto es el exceso enantiomérico obtenido. La adición de pequeñas cantidades de estaño (Sn/Pt= 0.01) produce un ligero incremento en la velocidad de hidrogenación inicial, y al mismo tiempo, un cambio relativamente pequeño en el valor de ee%. Cantidades más altas de estaño, generan una disminución en la velocidad inicial de hidrogenación, junto con una marcada disminución del ee.*

### Introduction

Transition metals are active, in general, as hydrogenation catalysts [1, 2], although, sometimes this property makes them to be non specific. For this reason, in order to improve their selectivity towards a certain function, different strategies are used. Among them, perhaps, the most common one is the addition of a second metal as promoter giving rise to bimetallic systems. Our research group has successfully obtained PtSn bimetallic systems, very active and selective in the hydrogenation of carbonyl compounds, employing techniques derived from the so called Surface Organometallic Chemistry on Metals (SOMC/M) [3].

A special kind of hydrogenation reaction is the one involving optically pure products, named enantioselective hydrogenations. There exists a widespread coincidence

about the importance that these optically pure products have and they will have in becoming years in fields such as food, pharmaceutical and agrochemical industries. For this reason, special emphasis has been devoted to the development of catalytic processes conducting to optically pure compounds, or at least with high optical purity [4-6].

The enantioselective hydrogenation of  $\alpha$ -ketoesters is an outstanding reaction at industrial level, since the reaction products,  $\alpha$ -hydroxiesters, are important chiral intermediates for the synthesis of biologically active compounds, especially pharmaceuticals. Japanese researchers were the first ones that carried out studies in the field of asymmetric heterogeneous catalysis using Pt/C catalysts modified by cinchona alkaloids. These catalysts presented high optical yields, demonstrating the possibilities of obtaining enantioselective heterogeneous catalytic systems for the hydrogenation of  $\alpha$ -ketoesters [7]; from then on the hydrogenation of  $\alpha$ -ketoesters has been extensively studied. Another catalytic system that has been studied for the enantioselective hydrogenation of ethyl pyruvate, is that one formed by 5% Pt/Al<sub>2</sub>O<sub>3</sub> modified by dihydrocinchonidine and promoted with different tin amounts [8]. Results presented showed that the hydrogenation activity is suppressed completely at relatively low tin coverage (Sn/Pt < 0.06).

Those principles that govern the enantioselectivity on the catalyst surface have not been well established yet. Also, there exists scarce information about the catalyst structure, the enantio-differentiation mechanism and the specific function of the chiral modifier, and consequently this makes the progress to be limited.

In this work we study the behavior of monometallic Pt/SiO<sub>2</sub> and bimetallic PtSn/SiO<sub>2</sub> catalysts modified by cinchonidine, in the enantioselective hydrogenation of ethyl pyruvate. Bimetallic PtSn/SiO<sub>2</sub> catalysts are obtained by adding tin to monometallic Pt/SiO<sub>2</sub> by means of techniques derived from SOMC/M. In all the cases we analyze the effect of the metallic particle size, the concentration of chiral modifier (cinchonidine) and the concentration of the metallic promoter added (Sn) on both the enantiomeric excess (*ee*%) obtained and the catalytic activity.

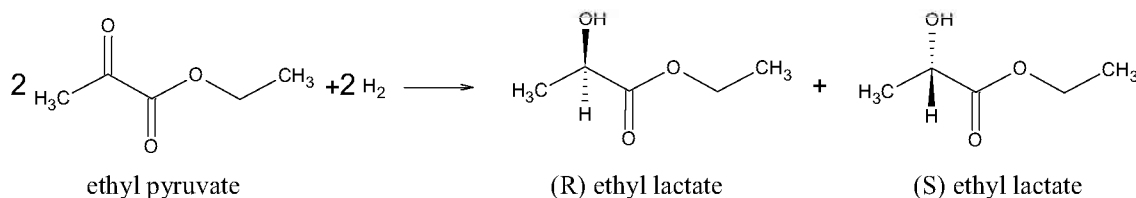
## Experimental

A SiO<sub>2</sub>-supported Pt catalyst having a content of 1%wt. Pt (denoted Pt/SiO<sub>2</sub> (A)) was prepared by ionic exchange with [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> (Aldrich), as it was described in previous papers [3]. The catalyst named Pt/SiO<sub>2</sub> (B) was generated upon sintering the base catalysts at 1073 K in flowing H<sub>2</sub> saturated with water at 298 K.

The bimetallic catalysts derived from the parent samples were designated PtSn<sub>x</sub>.x, being x.x an indication of the Sn/Pt atomic ratio (for instance, for Sn/Pt = 0.4 based on Pt/SiO<sub>2</sub> (A) catalyst, the notation would be PtSn<sub>0.4</sub> (A)). The preparation procedure for the bimetallic catalysts was the reaction of a SnBu<sub>4</sub> solution in n-heptane as solvent, with the reduced Pt/SiO<sub>2</sub> catalysts under flowing H<sub>2</sub>. 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 solid obtained after this procedure still had butyl groups grafted to the surface so, in order to obtain the bimetallic phase, the samples were activated in flowing H<sub>2</sub> at 773 K for 2 h. The concentration of the SnBu<sub>4</sub> solution was such so as to obtain the desired Sn/Pt atomic ratio in the resulting catalyst.

Catalysts were characterized by H<sub>2</sub> and CO chemisorption, Transmission Electronic Microscopy (TEM) and Temperature Programmed Reduction (TPR). The chemisorbed amount of H<sub>2</sub> or CO on the platinum surface (expressed as H/Pt and CO/Pt, respectively) was calculated by using the double isotherm method. The difference between the two isotherms, extrapolated at zero pressure, represents the irreversibly adsorbed H<sub>2</sub> or CO. A Jeol 100 CX electron microscope with side entry goniometer was used to determine the average particle diameter (dTEM). The average particle size was calculated by the expression  $d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$ , where  $n_i$  is the number of particles with size  $d_i$ . TPR of the catalysts was performed using conventional dynamic equipment. The H<sub>2</sub>/N<sub>2</sub> feed flow ratio was 1/9 and the heating rate was 10 K.min<sup>-1</sup> from room temperature to 1273 K.

The hydrogenation of ethyl pyruvate (Fluka) was performed in a batch reactor (Autoclave Engineers) at a H<sub>2</sub> pressure of 1.0 MPa and 313 K, employing 0.25 g of catalyst and isopropyl alcohol as solvent. The reaction progress was followed by sampling a sufficient number of micro samples. The composition of the samples was analyzed with a Varian GC 3400 gas chromatograph, equipped with a CP-Chirasil-Dex CB capillary column and a flame ionization detector. The only reaction products, (R) and (S) ethyl lactate, were completely separated under the conditions used.



The enantiomeric excess,  $ee$ , of each sample was calculated using the equation:

$$ee\% = \frac{([R] - [S])}{([R] + [S])} \times 100 \quad (1)$$

**Catalyst modification:** A chiral substance, in this case, cinchonidine, is adsorbed onto the catalyst surface. In the modification process, the catalyst was not exposed to air at any stage. A sample of a reduced catalyst was placed in a quartz reactor under H<sub>2</sub> atmosphere at 298 K. A measured volume of a cinchonidine solution was added via a septum into the reactor. The catalyst and the modifier were stirred for 18 h under flowing H<sub>2</sub>, then, the solution was decanted and the wet catalyst was washed into the batch reactor with a further 80 mL isopropyl alcohol to carry out the hydrogenation of 2 mL of ethyl pyruvate. The cinchonidine concentration in solution (Fluka) was measured spectrophotometrically, using the band at 283 nm ( $\epsilon = 5560 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ).

## Results and discussion

### Characterization

Characterization data of the two Pt/SiO<sub>2</sub> catalysts employed, Pt/SiO<sub>2</sub>(A) and Pt/SiO<sub>2</sub>(B), and one bimetallic catalyst (PtSn<sub>0.4</sub>(A)) are summarized in Table 1. TEM measurements indicate that the particle size distribution of Pt/SiO<sub>2</sub>(A) is very narrow, with a mean particle diameter of *c.a.* 2.4 nm. The treatment of Pt/SiO<sub>2</sub>(A) at 1073 K in H<sub>2</sub> saturated with water resulted in the sintering of the platinum particles to a value of

$d_{\text{TEM}} = 6.2$  nm (Pt/SiO<sub>2</sub> (B)). Chemisorption results are in agreement with the dispersion values calculated by TEM. Concerning bimetallic PtSn/SiO<sub>2</sub> catalysts, several samples were prepared having different tin contents. Results of their characterization can be summarized as follows: as it is shown in Table 1, for PtSn<sub>0.4</sub>(A) the tin addition on all catalysts produced a slight increase in the particle size measured by TEM, which cannot be assigned to the sintering of the platinum phase, but to the selective deposition of tin onto this phase. In agreement with these results, bimetallic catalysts exhibited an important decrease of their chemisorption capacity (both for H<sub>2</sub> and CO), which also suggests a very selective interaction of Sn with Pt.

**Table 1:** Characterization by TEM, chemisorption of H<sub>2</sub> and TPR of some tested catalysts

Catalyst	$d_{\text{TEM}}$ (nm)	H/Pt	Tpeak (K)
Pt/SiO <sub>2</sub> (A)	2.4	0.60	390-700
Pt/SiO <sub>2</sub> (B)	6.2	0.21	390-700
PtSn <sub>0.4</sub> (A)	2.9	0.21	430-700

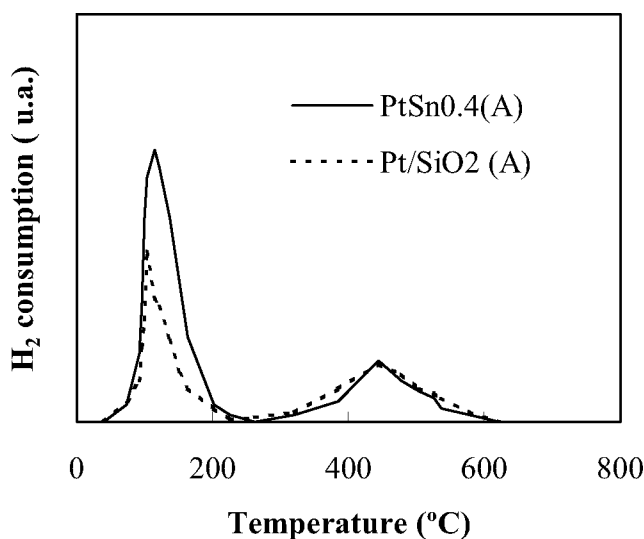
TPR profiles consisted of two peaks of H<sub>2</sub> consumption, whose temperatures are indicated in Table 1: a first one, at low temperature, assigned to platinum oxides having a relatively weak interaction with the support, and another peak at a higher temperature corresponding to platinum oxides with a stronger interaction with the support. For all PtSn/SiO<sub>2</sub> catalysts, an increase in the area of the low temperature peak was observed in the TPR assay, which can be assigned to the reduction of platinum oxides and a fraction of tin oxides (see Figure 1). This fact can be explained considering that platinum, near tin, dissociates the H<sub>2</sub> employed in the tin reduction.

### Catalytic tests

#### Unmodified catalysts

The ethyl pyruvate hydrogenation using Pt/SiO<sub>2</sub>(A), Pt/SiO<sub>2</sub>(B), PtSn<sub>0.4</sub>(A) and PtSn<sub>0.4</sub>(B) catalysts was carried out without the addition of the chiral modifier cinchonidine in order to analyze their hydrogenating capacity. Figure 2 shows results obtained. The analysis of the behavior of monometallic catalysts shows that the initial reaction rate increases as the size of metallic particles increases, in agreement with previously published experimental and theoretical studies [9-12]. The values of the initial rate obtained for these catalysts are shown in Table 2. Tin addition increases the hydrogenation rate of the ethyl pyruvate with respect to the corresponding monometallic catalyst; being this increment more important for catalysts having higher dispersion (when the size of metallic particles decreases). This effect has already been detected in other carbonyl compound and it is assigned to the coexistence of effects of geometric nature ("isolation" of the platinum sites that favors the adsorption of the substrate molecule "on top" on these sites, via the oxygen atom of the C=O group) and of electronic nature, since, as it has been previously published, this type of bimetallic

catalysts presents a fraction of tin in ionic state giving rise to Lewis acid sites that favor the activation of the C=O group, and so its hydrogenation to C-OH [3].



**Figure 1:** TPR for monometallic and bimetallic catalysts (for conditions see the text).

**Table 2:** Initial reaction rate for the hydrogenation of ethyl pyruvate on different Pt and PtSn unmodified catalysts. Experimental conditions are: 1.0 MPa hydrogen pressure, 313 K, 0.25 g catalyst, 2mL ethyl pyruvate, 80 mL isopropyl alcohol (solvent).

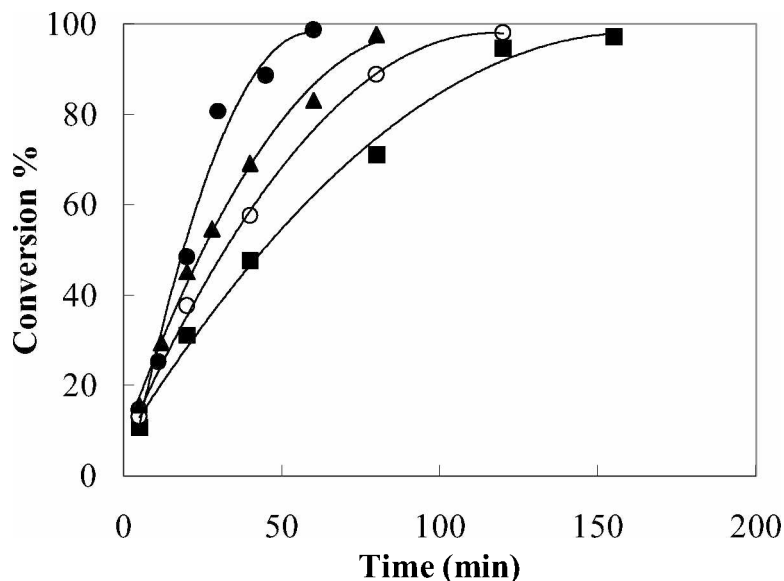
Catalyst	Initial reaction rate mmol.g <sub>Pt</sub> <sup>-1</sup> .s <sup>-1</sup>
Pt/SiO <sub>2</sub> (A)	2.65
Pt/SiO <sub>2</sub> (B)	3.48
PtSn0.4/SiO <sub>2</sub> (A)	4.87
PtSn0.4/SiO <sub>2</sub> (B)	4.20

With respect to the enantioselectivity of these catalytic systems, in all cases, a racemic mixture of ethyl lactates was obtained as product of the ethyl pyruvate hydrogenation, since there was no chiral modifier in the reaction mixture.

#### *Enantioselective hydrogenation of ethyl pyruvate*

The cinchonidine addition to the reaction system, in all hydrogenation experiments, permits the obtention of an excess of (R)-ethyl lactate over the (S)-ethyl lactate. The preferential formation of one of the optical isomers can be explained by the so called "template mechanism", proposed by Sutherland et al. [13]. According to this model, the cinchonidine molecule conformation that generates the system of lowest energy content, is the one in which the molecule is adsorbed on the superficial platinum through the quinoline aromatic system, utilizing an L-shaped region of the surface, thus

blocking totally a series of active sites and partially other sites due to quinuclidine system presence. This geometrical disposition would be responsible for the fact that ethyl pyruvate molecules could contact a limited portion and for a peculiar geometry of the platinum surface, in such a way that the hydrogenation of these molecules would be restricted to those that can be adsorbed under these conditions, which generates in turn, the corresponding restriction in the product formed. The majority of ethyl pyruvate molecules present in the reaction solution is adsorbed on sites, which, on reaction, produce (R)-ethyl lactate.



**Figure 2:** Hydrogenation of ethyl pyruvate on nonmodified catalysts. Activity as a function of time for the following catalysts: (■) Pt/SiO<sub>2</sub> (A), (○) Pt/SiO<sub>2</sub> (B), (●) PtSn (A) 0.4, (▲) PtSn (B) 0.4 (Experimental conditions are: 1.0 MPa hydrogen pressure, 313 K, 0.25 g catalyst, 2mL ethyl pyruvate, 80 mL isopropyl alcohol (solvent))

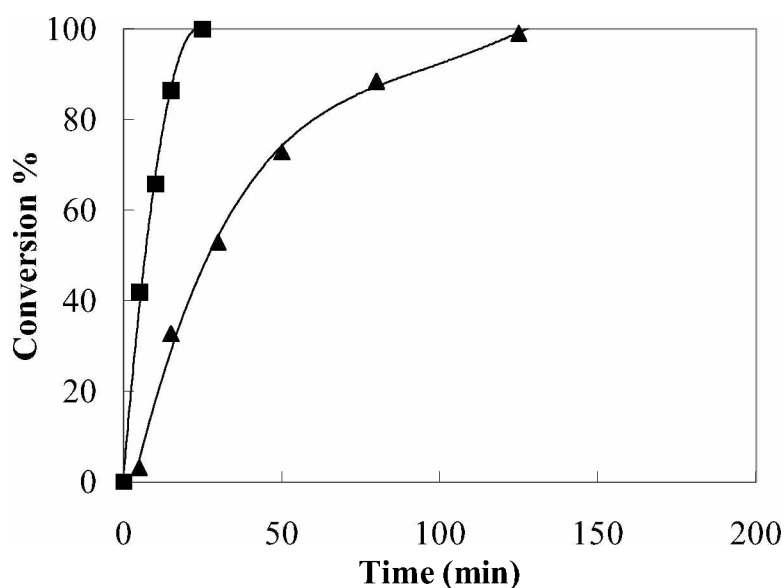
The influence of different experimental parameters on the enantioselective hydrogenation of ethyl pyruvate was analyzed. To study the effect of the metallic particle size, both Pt/SiO<sub>2</sub>(A) and Pt/SiO<sub>2</sub>(B) monometallic catalysts were modified with cinchonidine. In Table 3 results are gathered for the cinchonidine modified catalysts.

The cinchonidine concentration employed to modify the catalysts was changed in order to analyze if it would have any influence either upon the enantiomeric excess or on the hydrogenation rate, or on both. In every studied case, the addition of cinchonidine provokes an increase in the hydrogenation rate of ethyl pyruvate, as shown in Table 3. These results agree, among others, with results of Blaser et al., who have reported the increase in the hydrogenation rate of ethyl pyruvate on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts modified with quinuclidine [14]. Besides, it is well-known that the addition of bases such as cinchonidine (pK<sub>a</sub> = 8.3) increases the hydrogenation rate of a ketonic carbonyl due to the donor effect of the lone pair of electrons of the nitrogen atom. The increment is more

noticeable in the system with higher dispersion (Pt/SiO<sub>2</sub>(A)), as it can be observed in Figure 3 for the so designated Pt/SiO<sub>2</sub>(AC2) and Pt/SiO<sub>2</sub>(BC2) catalysts modified with a 0.0188 M cinchonidine solution.

**Table 3:** Enantioselective hydrogenation of ethyl pyruvate: effect of cinchonidine concentration. Experimental conditions are: 1.0 MPa hydrogen pressure, 313 K, 0.25 g catalyst, 2mL ethyl pyruvate, 80 mL isopropyl alcohol (solvent), ee % measured at 90 % conversion.

Catalyst	Cinchonidine concentration (M)	ee%	Initial rate of hydrogenation (mmol.g <sub>Pt</sub> <sup>-1</sup> s <sup>-1</sup> )
Pt/SiO <sub>2</sub> (B)	0	0	3.48
Pt/SiO <sub>2</sub> (BC1)	0.0094	53	9.50
Pt/SiO <sub>2</sub> (BC2)	0.0188	64	9.28
Pt/SiO <sub>2</sub> (BC3)	0.0375	60	9.80
Pt/SiO <sub>2</sub> (A)	0	0	2.65
Pt/SiO <sub>2</sub> (AC1)	0.0094	15	6.70
Pt/SiO <sub>2</sub> (AC2)	0.0188	30	11.50
Pt/SiO <sub>2</sub> (AC3)	0.0375	31	10.10



**Figure 3:** Enantioselective hydrogenation ethyl pyruvate on catalysts modified with a 0.0188 M cinchonidine solution. Activity as a function of time for the following catalysts: (■) Pt/SiO<sub>2</sub> (AC2), (▲) Pt/SiO<sub>2</sub> (BC2) (Experimental conditions are: 1.0 MPa hydrogen pressure, 313 K, 0.25 g catalyst, 2mL ethyl pyruvate, 80 mL isopropyl alcohol (solvent)).

With regard to the enantiomeric excess, the ee% value increases steeply with reaction time up to 10 % conversion and then keeps constant until reaction is finished.

The ee% values level off with increasing cinchonidine concentration; lower values obtained for the lower cinchonidine concentration may be probably assigned to an incomplete chiral modification of the platinum surface. The isopropyl alcohol presence in the reaction mixture may also have certain influence on these results, since cinchonidine is considerably soluble in alcohol. For this reason, a fraction of the modifier could be possibly removed from the surface by the solvent, and in that case, its adsorbed concentration would not be enough to act as an efficient chiral modifier. These results agree with those presented, among others, by Wehrli *et al* for the ethyl pyruvate hydrogenation using acetic acid as solvent and with results of Borszky *et al* for the hydrogenation of 2-methyl-2-pentenoic acid over cinchonidine-modified Pd/Al<sub>2</sub>O<sub>3</sub>. However, they are significantly different from results presented by LeBlond, with methylbenzene as solvent that showed a volcano type curve [15-17]. The variety of results demonstrates the complexity of these systems and that the behavior of these catalytic systems depends on a large number of factors.

A value of ee% = 30 was obtained with Pt/SiO<sub>2</sub> (AC2) catalyst while with Pt/SiO<sub>2</sub> (BC2) catalyst, a ee% = 64 was reached, illustrating the importance of the particle size upon the chiral hydrogenation capacity of catalysts. These results may be explained taking into account that the adjacent adsorption of the big cinchonidine molecule and a molecule of ethyl pyruvate occupy a considerable space on the catalyst surface (approximately between 10 and 20 atoms of Pt). According to this fact, it seems reasonable that the enantioselectivity should depend on the metallic particle size of the catalyst. Results obtained in the present work, in which catalysts employed had mean particle sizes 2.5 nm (Pt/SiO<sub>2</sub> (AC2)) and 6.2 nm (Pt/SiO<sub>2</sub> (BC2)), confirm the existence of this effect. Similar results have been presented by Wells and Wilkinson [18].

Platinum/tin systems are very well-known hydrogenation catalysts. In order to investigate their performance as enantioselective catalysts, different PtSn bimetallic catalysts modified by the cinchonidine addition were tested in the ethyl pyruvate hydrogenation. PtSn catalysts were obtained by application of the SOMC/M techniques that have proven to be very effective for the introduction of very small tin amounts on the reduced platinum in a selective way.

**Table 4:** *Enantioselective hydrogenation of ethyl pyruvate on different PtSn catalysts. Experimental conditions are: 1.0 MPa hydrogen pressure, 313 K, 0.25 g catalyst, 2mL ethyl pyruvate, 80 mL isopropyl alcohol (solvent), cinchonidine concentration 0.0188 M, ee % measured at 90 % conversion.*

Catalyst	Sn/Pt atomic ratio	Initial rate (mmol <sub>gPt</sub> <sup>-1</sup> s <sup>-1</sup> )	ee%
Pt/SiO <sub>2</sub> (BC2)	0	9.28	64
PtSn0.01 (BC2)	0.01	9.86	54
PtSn0.02 (BC2)	0.02	6.41	44
PtSn0.04 (BC2)	0.04	3.81	13
PtSn0.4 (BC2)	0.4	3.74	0
PtSn0.01 (AC2)	0.01	3.44	33



In Table 4, results obtained for the different analyzed catalysts are gathered. With regard to the activity, it is observed that a small tin amount (Sn/Pt = 0.01) produces a slight increment in the initial hydrogenation rate, and at the same time, a relative small change of the enantiomeric excess. An increment in the added tin amount produces a decrease in the initial hydrogenation rate, together with a marked diminution of the enantiomeric excess. These results would be indicating that the tin presence diminishes markedly the number of available platinum sites of the surface, so that cinchonidine molecules cannot be adsorbed in a very efficient way. Besides, tin and cinchonidine would be competing as electron donors towards platinum atoms. These two facts would be responsible for the decrease of the cinchonidine molecule effectiveness as a chiral inductor (giving lower *ee*% values) on one hand, and on the other hand, for limiting the charge of negatively polarized platinum atoms (previously measured by XPS [3]), thus diminishing the hydrogenation rate of the ethyl pyruvate.

## Conclusions

The hydrogenation of ethyl pyruvate on Pt/SiO<sub>2</sub> without chiral modifier in the reaction mixture shows that the initial reaction rate increases as the size of metallic particles increases. The cinchonidine addition generates an increment in the reaction rate in a factor of approximately 4.

The cinchonidine addition to the reaction system, in all hydrogenation experiments, permits the obtention of an excess of (R)-ethyl lactate over the (S)-ethyl lactate isomer. This excess shows a strongly dependence with the mean particle size of Pt in monometallic catalysts. Pt/SiO<sub>2</sub> (A) catalyst (dp = 2.5 nm) reaches a *ee*% = 30, while with Pt/SiO<sub>2</sub> (B) catalyst (dp = 6.2 nm) an *ee*% = 64 is obtained. For the studied concentration interval, the cinchonidine concentration does not show any influence either for *ee* or on the reaction rate.

A small amount of tin added (Sn/Pt = 0.01) produces a slight increment in the initial hydrogenation rate, and at the same time, a relative small change in the *ee*% value. An increase in the amount of tin added generates a decrease in the initial hydrogenation rate, together with a marked diminution of the *ee* value.

Taking into account all the results obtained it could be stated that the best system among those studied is Pt/SiO<sub>2</sub> (BC2).

## 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 N° 14-04378, Argentina.

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