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Use of (*S*)-(+)-1-aminoindan, (*S*)-(+)-1-indanol and (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol as chiral modifiers in the enantioselective hydrogenation of ethyl pyruvate with Pt/SiO_2 catalysts

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Abstract

In this work it is studied the enantioselective hydrogenation of ethyl pyruvate using a Pt/SiO_2 catalyst, modified with different chiral auxiliaries: (*S*)-(+)-1-aminoindan, (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol and (*S*)-(+)-1-indanol. Cinchonidine modified system was taken as reference. It is analyzed the influence of the particle size of the catalyst, the molecular structure of the modifier and the nature of the solvent. The enantioselective hydrogenation of ethyl pyruvate resulted to be a structure-sensitive reaction, and accordingly, the Pt/SiO_2 (B) catalyst (dp = 6.5 nm) provided the best results. The modifier (*S*)-(+)-1-aminoindan presented an ee of 63%, whereas (*S*)-(+)-1-indanol gave a racemic mixture and (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol showed an effect of "erosion of enantiomeric excess". Concerning the solvent, a higher ee in 2-propanol was obtained when the modifier used was the (*S*)-(+)-1-aminoindan, while in toluene, *n*-heptane and acetic acid the performance of the catalytic systems was not good.

Keywords: Pt/silica; Heterogeneous catalyst; Enantioselective hydrogenation; Ethyl pyruvate; Aminoindan; 2-Propanol; Toluene

1. Introduction

The obtention of optically pure compounds has gained importance at the present time towards the generation of pharmaceutical products, flavors, fragrances and agrochemical agents. Up to the moment, the most effective way to generate enantiopure chemical products is through the asymmetric synthesis, in which the homogeneous catalysis plays a fundamental role. However, the development of heterogeneous catalysts for these types of processes are more and more important each day, due to their recognized advantages with respect to handling, separation, stability and recovery [1–3].

Several methods have been introduced to develop heterogeneous chiral catalysts, especially taking into account the capacity of separating and recycling the catalyst. Some reviews have appeared in the literature describing different types of immobilization techniques, such as the attachment of chiral ligands either onto or into a support material [4]. The method developed by Augustine et al. to prepare heterogeneous chiral catalysts, consists on anchoring a metallic complex onto a support using a heteropolyacid as intermediate. This technique has proved to be especially adequate for applications of enantioselective catalysis employing immobilized Rh complexes with chiral diphosphines as ligands [5]. Finally, in our research group, it has been developed a methodology to obtain heterogeneous chiral catalysts, based on the application of surface organometallic chemistry on metals. The catalysts so-obtained, resulted to be chemo- and enantioselective for the hydrogenation of aromatic ketones [6,7].

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The so-called ‘‘classic approximation’’ to obtain heterogeneous enantioselective catalysts, consists on using chiral compounds to modify a heterogeneous metallic catalyst. This methodology allowed, by the end of the 1970s, the development of the most employed heterogeneous chiral catalysts: Ni catalyst modified with sodium tartarate/NaBr used for the hydrogenation of β-ketoesters [8,9] and Pt(Pd) modified with alkaloids of the cinchona group used to hydrogenate α-ketoesters ([10] and references therein). The enantioselective hydrogenation of α-ketoesters constitutes a useful reaction at industrial level since the reaction products, α-hydroxyesters, are key intermediates in the synthesis of biologically active compounds [11]. Japanese researchers were the first ones in performing studies in the field of asymmetric catalysis using Pt/C catalysts modified with cinchonidine for the hydrogenation of ethyl pyruvate obtaining high optical yields [12].

A generalization about the explanation of the mechanism of the asymmetric induction in these types of catalytic systems, is not yet existent, probably due to the complexity of the system: metallic catalyst/chiral modifier/substrate/solvent. All these four parameters have to be optimized to achieve high optical yields, but this has to be accomplished taking into account the important interactions among them [13]. With respect to the nature of the chiral modifier, when analyzing the performance of Pt-based catalysts modified with cinchonidine, the effectiveness in the obtention of high enantiomeric excesses is assigned to the cinchonidine structure, in which three crucial factors are present: a group capable of anchoring the molecule onto the surface of the metallic catalyst, the presence of a basic nitrogen atom near the stereogenic center and a chiral center [14].

(1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol has been employed combined with chirally modified Rh(I), Ir(I) and Ru(II) complexes to provide an efficient catalyst for the asymmetric transfer hydrogenation of acetophenone with 2-propanol to produce (*R*)- and (*S*)-1-phenylethanol [15,16]. In the present work, it is reported the use of (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol as chiral modifier of a heterogeneous platinum catalyst. This molecule presents in its structure the three above-mentioned characteristics of cinchonidine, but it is, comparatively simpler and more rigid than cinchonidine. (*S*)-(+)-1-indanol and (*S*)-(+)-1-aminoindan were also selected as chiral modifiers. All the modifiers employed are represented in Fig. 1.

As other objective of this work, they will be studied the influence of particle size of the base metallic catalyst and the solvent nature on the reaction rate and the enantiomeric excess (ee%) in the enantioselective hydrogenation of ethyl pyruvate using a Pt/SiO_2 catalyst modified with (*S*)-(+)-1-aminoindan.

2. Experimental

2.1. Catalyst preparation

A non-porous silica from Degussa (Aerosil 200, 200 $m^2 g^{-1}$) was used as support. This silica was suspended in NH_4OH(aq), maintaining it under stirring up to the addition of $[Pt(NH_3)_4]Cl_2$ (Aldrich), employed as platinum precursor. The concentration of the $[Pt(NH_3)_4]Cl_2$ solution was so as to

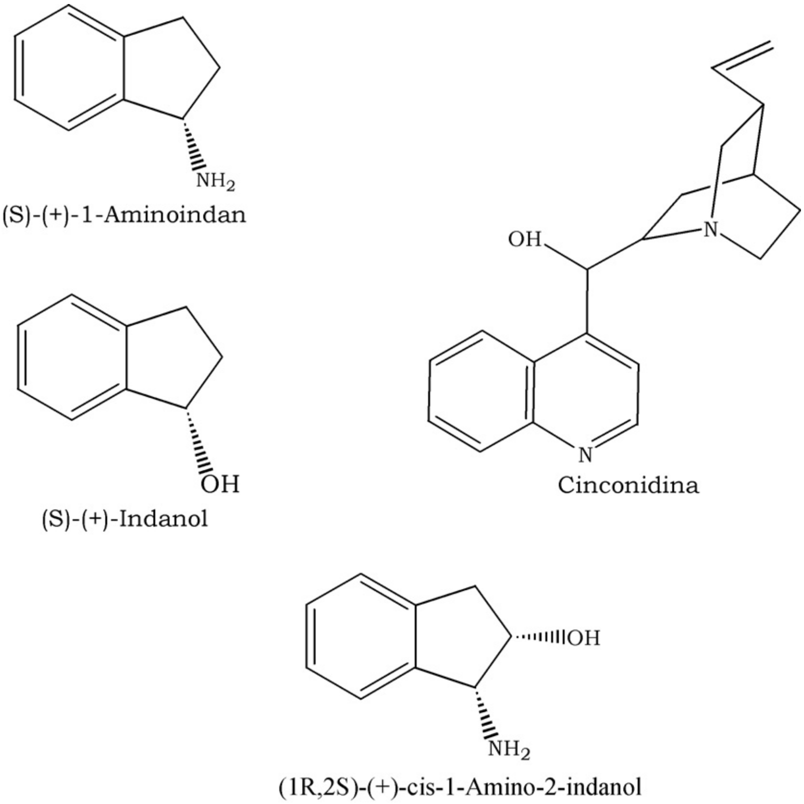

Fig. 1. Structures of the chiral modifiers studied.

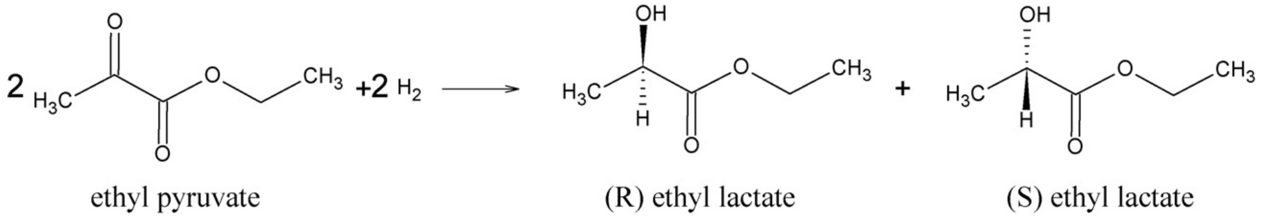

Fig. 2. Hydrogenation reaction of ethyl pyruvate.

obtain 2 wt.% Pt exchanged on the support. The solid was kept under stirring for 24 h at 298 K and then it was separated from the solution by vacuum filtration. The solid was washed repeatedly, dried at 378 K, calcined in air at 773 K and reduced in H_2 flow at the same temperature, leading to the monometallic catalyst Pt/SiO_2 (A).

The catalyst named Pt/SiO_2 (B) was obtained by a sintering process of the catalyst Pt/SiO_2 (A), by means of a treatment in H_2 flow saturated with water vapor for 5 h at 1073 K. Before its use in the hydrogenation reaction, it was reduced at 773 K for 2 h in pure H_2.

2.2. Catalyst characterization

The platinum content was determined by atomic absorption spectroscopy. The distribution of metallic particle sizes was determined by transmission electron microscopy (TEM) using a JEOL 100 CX instrument. The samples were ground and ultrasonically dispersed in distilled water. To estimate the mean particle size, the particles were considered spherical and the second moment of the distribution was employed. The expression used for the calculation was

$$d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where n_i is the number of particles with d_i size.

Temperature programmed reduction tests (TPR) were carried out in a conventional reactor equipped with a thermal conductivity detector with a feeding flow of 20 $cm^3\ min^{-1}$ (10% H_2 in N_2) at a heating rate of 10 K min^{-1}.

2.3. Catalyst modification

On a reduced sample of Pt/SiO_2 catalyst, 10 mL of a 0.03 M solution of the corresponding modifier (*S*)-(+)-1-aminoindan, (*S*)-(+)-1-indanol, (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol (Aldrich) or cinchonidine (Fluka) were added and the systems were left in contact for 24 h.

2.4. Hydrogenation reactions

The hydrogenation reaction of 1 mL ethyl pyruvate (Aldrich) (Fig. 2) was performed in an autoclave type reactor (Autoclave Engineers), at 1.0 MPa H_2 pressure and at a temperature of 273 K, using 0.25 g catalyst and 60 mL solvent. The reaction advance was followed by gas chromatography in a Varian GC 3400 chromatograph equipped with a capillary column (CP–Chirasil–Dex CB) and a FID detector. The only reaction products obtained, (*R*) and (*S*)-ethyl lactate, were completely separated under the analysis conditions used.

The enantiomeric excess (ee%) was calculated using the following expression:

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

3. Results and discussion

3.1. Catalyst characterization

Characterization results for catalysts Pt/SiO_2 (A) and Pt/SiO_2 (B) are presented in Table 1. TEM results indicate that for the Pt/SiO_2 (A) catalyst, the particle size distribution is narrow, centered around dp = 2.5 nm. Pt/SiO_2 (B) catalyst (obtained by treatment of Pt/SiO_2 (A) in H_2 saturated with water vapor at 1073 K), presented an average particle size of about 6.5 nm. TPR spectra show similar characteristics for both studied catalysts, presenting two H_2 consumption peaks, whose temperatures are indicated in Table 1: one reduction peak at a lower temperature, around 430 and 460 K for Pt/SiO_2 (A) and Pt/SiO_2 (B), respectively, and a second one at higher temperatures (690 and 715 K). These results show the existence of different species of platinum that are reduced at different temperatures [17]. The first peak can be assigned to the reduction of platinum oxide dispersed on the support [18]. The second peak can be assigned either to the reduction of Pt(IV) to Pt(0) or it could be also assigned to the presence of platinum oxychlorides species (PtO_xCl_y) [19–21].

3.2. Hydrogenation of ethyl pyruvate

The addition of the modifiers cinchonidine, (*S*)-(+)-1-aminoindan and (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol to the reaction system, led to the obtention of an excess of (*R*)-ethyl lactate over (*S*)-ethyl lactate (when 2-propanol was used as

Table 1
Characterization of the platinum catalysts by TEM and TPR

Catalyst	d_{TEM} (nm)	T_{peak} (K)
Pt/SiO_2 (A)	2.5	430–690
Pt/SiO_2 (B)	6.5	460–715

solvent), and these substances resulted to be the only reaction products. When the added modifier was (*S*)-(+)-1-indanol, a racemic mixture was obtained.

3.2.1. *Influence of the particle size*

Enantioselective hydrogenations are structure-sensitive reactions requiring, in general, relatively big metallic particles to obtain an efficient enantiodifferentiation. The data available in the bibliography, indicate that for the ethyl pyruvate hydrogenation using cinchonidine as modifier, the adequate size of Pt particles has to be bigger than 3 nm [22], and similarly in the hydrogenation of a bigger molecule, 1-phenyl-1,2-propanedione, the optimum Pt particle size was found to be around 4 nm for Pt/Al_2O_3 catalysts [23] and 3.8 nm for Pt/SiO_2 [24]. Dispersions around 40% resulted beneficial in the hydrogenation of isophorone over (−)-dihydroapovincaminic acid ethyl ester modified Pd/C [25].

In the present work, in the first place, the hydrogenation of ethyl pyruvate using Pt/SiO_2 (A) and Pt/SiO_2 (B) catalysts was carried out without the addition of the chiral modifier, in order to analyze the existence of some kind of enantiomeric excess due to the different metallic particle size. The results presented in Table 2 show that with respect to the enantioselectivity, a racemic mixture of ethyl lactates was obtained as product. It is also observed that the initial reaction rate increases as the size of metallic particles increases, in agreement with previously published experimental and theoretical studies [26–29].

The enantioselective hydrogenation of ethyl pyruvate was analyzed at 273 K, using (*S*)-(+)-1-aminoindan as chiral modifier and 2-propanol as solvent. When the Pt/SiO_2 (A) catalyst was tested, the enantiomeric excess obtained was almost null, while with the Pt/SiO_2 (B) catalyst, under the same experimental conditions, the ee% value achieved was 63%. These results are in agreement with other ones previously obtained in our research group employing the same Pt-based catalysts, but modified with cinchonidine [30]. Such results showed that with the Pt/SiO_2 (A) catalyst, the ee% did not overcome 30%, while with the Pt/SiO_2 (B) catalyst the ee% value obtained was greater than 60% at 313 K.

A probable explanation for this situation can be found when taking into account that for an efficient interaction of the modifier/substrate system, a considerable space of the catalyst surface is required and, consequently, it is reasonable that the enantiomeric excess depends on the particle size of the catalyst [31].

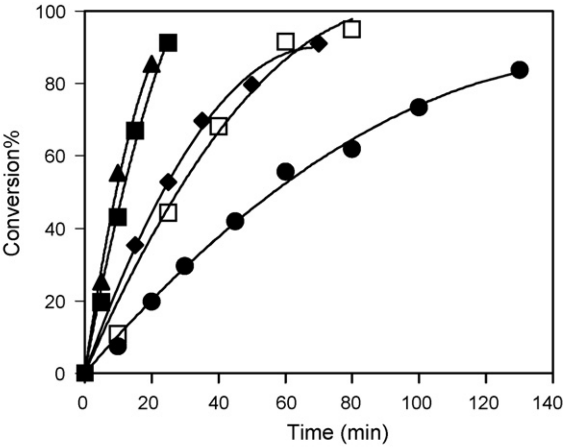

Fig. 3. Hydrogenation reaction of ethyl pyruvate in 2-propanol. Conversion as a function of time for the Pt/SiO_2 (B) catalyst. (□) Without modifier; and modified with: (▲) cinchonidine, (■) (*S*)-(+)-1-aminoindan, (◆) (*S*)-(+)-1-indanol and (●) (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol. (For experimental conditions, see the text).

According to the results obtained, the Pt/SiO_2 (B) catalyst was selected to continue with this study.

3.2.2. *Influence of the modifier structure*

Fig. 3 and Table 2 present results achieved in the racemic and enantioselective hydrogenation of ethyl pyruvate in 2-propanol as solvent, at 273 K, employing the Pt/SiO_2 (B) catalyst modified with different chiral inductors. When analyzing the activity of the different catalytic systems, it is possible to observe that the (*S*)-(+)-1-aminoindan presents a conversion around 90% for a reaction time of about 30 min, comparable with that obtained for cinchonidine. On the other hand, with the (*S*)-(+)-1-indanol, the conversion does not reach 70% and with the (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol it does not exceed 60% for the same reaction time (Fig. 3). The significant difference in the hydrogenation rate between aminoindan and aminoindanol can be interpreted on the basis of the existence of an important interaction between –OH and –NH_2 groups in the aminoindanol molecule. This "intramolecular hydrogen bridge" seems to inhibit the effective interaction between the modifier and the substrate and, so, the hydrogenation of the ethyl pyruvate is even slower than its racemic hydrogenation and, also, the ee% obtained is low (Table 2). A similar effect was observed by Cserényi et al. in the

Table 2
ee%, absolute configuration and reaction rate for the hydrogenation of ethyl pyruvate at 1.0 MPa of H_2 pressure, 273 K, 2-propanol and 0.25 g catalyst

Catalyst	Chiral modifier	ee%[*]	r_i[**] ($\text{mmol}\,\text{g}_{\text{PtSuperficial}}^{-1}\,\text{s}^{-1}$)
Pt/SiO_2 (A)	–	–	1.22
Pt/SiO_2 (B)	–	–	2.96
Pt/SiO_2 (B)	Cinchonidine	64 (*R*)	7.97
Pt/SiO_2 (B)	(*S*)-(+)-1-Aminoindan	63 (*R*)	7.35
Pt/SiO_2 (B)	(1*R*, 2*S*)-(+)-*cis*-1-Amino-2-indanol	<5 (*R*)	1.89
Pt/SiO_2 (B)	(*S*)-(+)-1-Indanol	–	3.68

[*] ee% measured at 80% conversion.
[**] Reaction rate estimated between 0% and 10% conversion.

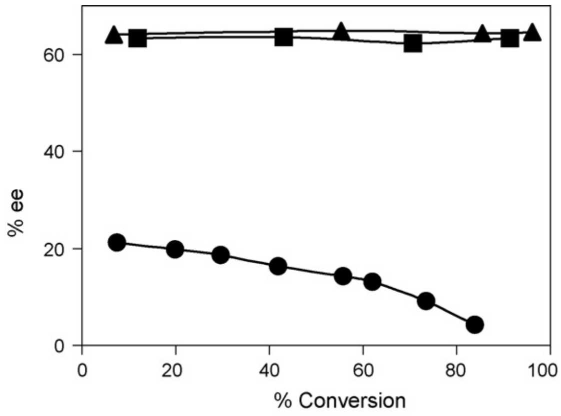

Fig. 4. Hydrogenation reaction of ethyl pyruvate in 2-propanol. ee% as a function of conversion for Pt/SiO$_2$ (B) catalyst modified with: (▲) cinchonidine, (■) (*S*)-(+)-1-aminoindan and (●) (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol. (For experimental conditions, see the text).

hydrogenation of ethyl pyruvate with different cinchonidine derivatives [32,33].

With respect to the enantiomeric excess, different modifiers showed distinct behaviors. Thus, while the (*S*)-(+)-1-aminoindan allowed to obtain a ee% of 63% at 80% conversion (behaving in a similar way as the system that uses cinchonidine as modifier, ee% = 64), the (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol led to values of ee below 5%, and the (*S*)-(+)-1-indanol gave a racemic mixture as product, at the same conversion level (Table 2). Therefore, the presence and the positioning of the basic nitrogen atom determines the obtention of an ee and a higher reaction rate. The necessity for a basic nitrogen atom is inferred from the fact that its absence in (*S*)-(+)-1-indanol leads to racemic ethyl lactate. This behavior is analogous to the one observed when the nitrogen atom of the quinuclidine moiety of cinchonidine is alkylated, and so, the optical induction is lost completely [14].

In measurements performed with (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol, ee% values of *ca.* 20% where observed up to 45 min reaction, but it decayed as the reaction time was longer (Fig. 4). This "erosion" of the enantiomeric excess has also been observed by other authors in different enantioselective catalytic systems [15,34,35]. For instance, Le Blond et al., studying the case of the enantioselective hydrogenation of ethyl pyruvate with cinchonidine as modifier observed a decrease in the ee%, from 90% up to practically 0%, when the conversion increased from 0% up to 85% [35].

3.2.3. *Influence of the solvent*

The solvent effect on enantioselective hydrogenation reactions has been widely studied since, up to the moment, the attempts to generalize results in terms of solvent properties did not succeed [36]. The solvent nature affects system characteristics such as the activity, the selectivity, and the stereoselectivity, and several factors may be responsible for these variations: solubility of reagents, hydrogen solubility, competitive adsorption of solvent and reagent molecules on the catalytic surface, etc. [10]. Besides, complex organic molecules usually coexist in several conformations and the population of each one of the different conformers may vary as a function of the solvent dielectric constant, affecting the reaction selectivity [13]. Consequently, the solvent effect can be a combination of different physical and chemical phenomena and this makes difficult its complete explanation.

In the enantioselective hydrogenation reactions, the solvent polarity results to be of fundamental importance. For this reason, in the present work, the hydrogenation of ethyl pyruvate was tested in solvents of different polarity, analyzing the changes produced in the ee obtained and in the reaction rate (Table 3 and Fig. 5a and b). The basis of the comparative study was the catalytic systems modified with cinchonidine. In this case, a value of ee% over 90% was obtained in acetic acid that resulted to be higher than when toluene (81%) and 2-propanol (64%) were used. The reaction rate followed the same tendency for these two last solvents, but it should be underlined that in the case of acetic acid, while the ee% was the highest of the three, the reaction rate was the lowest (Fig. 5a). This result is in agreement with what is found in the literature for these types of systems, and is generally explained as a function of the interaction degree of the nitrogen atom of the quinuclidine moiety of cinchonidine with the substrate. It is postulated that the difference between the enantioselective hydrogenation of ethyl pyruvate in toluene and in acetic acid passes through the structures of the intermediates responsible for enantioselection

Table 3
ee%, absolute configuration and reaction rate for the enantioselective hydrogenation of ethyl pyruvate at 1.0 MPa of H$_2$ pressure, 273 K, 0.25 g of Pt/SiO$_2$ (B) catalyst and different solvents

Modifier	Solvent	ee%[a]	r_i[b] (mmolg$_{\mathrm{PtSuperficial}}^{-1}$ s^{-1})	ε[d]
Cinchonidine	2-Propanol	64 (*R*)	7.97	18.3
	Toluene	81 (*R*)	9.57	2.0
	Acetic acid[c]	>90 (*R*)	1.68	6.2
(*S*)-(+)-1-Aminoindan	2-Propanol	63 (*R*)	7.35	18.3
	Toluene	13 (*S*)	4.40	2.0
	n-Heptane	14 (*S*)	1.56	1.9
	2-Propanol + trifluoroacetic acid	5 (*R*)	0.05	–
	Acetic acid[c]	10 (*R*)	1.68	6.2

[a] ee% measured at 80% conversion.
[b] Reaction rate estimated between 0% and 10% conversion.
[c] Reaction temperature = 293 K.
[d] Dielectric constant.

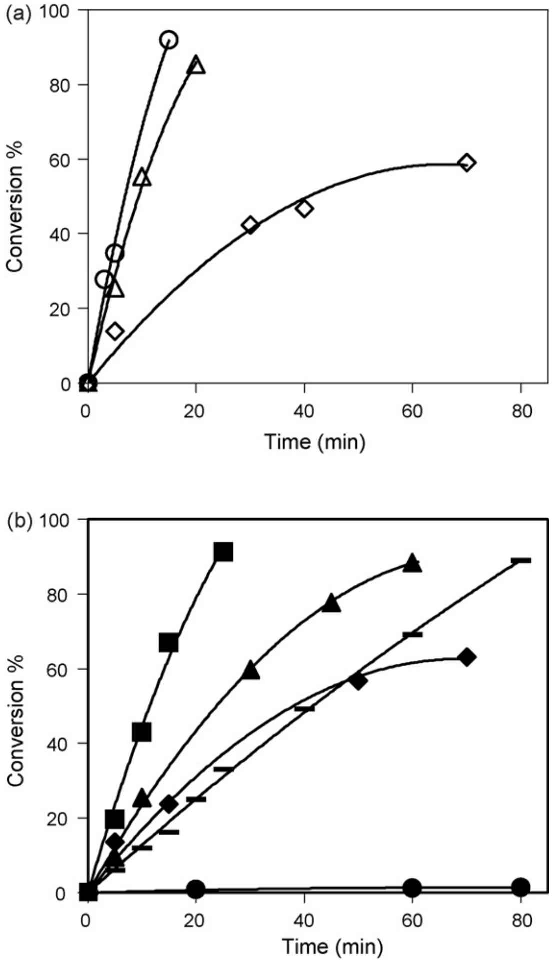

Fig. 5. (a) Effect of the solvent in the hydrogenation of ethyl pyruvate with Pt/SiO_2 (B) catalyst modified with cinchonidine: (○) toluene, (△) 2-propanol and (◇) acetic acid (293 K). (For experimental conditions, see the text). (b) Effect of the solvent in the hydrogenation of ethyl pyruvate with Pt/SiO_2 (B) catalyst modified with (*S*)-(+)-1-aminoindan: (■) 2-propanol, (▲) toluene, (●) 2-propanol + trifluoroacetic acid, (—) *n*-heptane and (◆) acetic acid (293 K). (For experimental conditions, see the text).

[13,37–41]. In a scarcely polar solvent like toluene, a half-hydrogenated ethyl pyruvate molecule is supposed to get bonded to the nitrogen of quinuclidine, *via* a hydrogen bond. The hydrogen source is the hydrogen dissociatively adsorbed on the platinum. In an acid solvent like acetic acid, ethyl pyruvate is bonded to the protonated quinuclidine *via* a hydrogen bond.

As it is shown in Table 3, systems modified with (*S*)-(+)-1-aminoindan showed an inverse behavior. To correlate the ee% obtained with the characteristics of the solvents, we have used the dielectric constant, but a similar behavior is obtained using other parameters, such as the empirical solvent parameter E_T^N [42]. The highest ee% value to (*R*)-ethyl lactate was obtained for 2-propanol (63%), a solvent with a significant polarity. The ee% decreased for the less polar solvents toluene and *n*-heptane, being also observed that the ee inverted from the (*R*) to the (*S*) enantiomer. This behavior may be an indication of a significant change in the reaction mechanism. The inversion of the enantioselectivity when changing the solvent is not an unusual fact in asymmetric hydrogenation reactions. One example coming from homogeneous catalysis include the hydrogenation of dehydroamino acid derivatives with Rh(I) complexes [43]. There are also some reports of heterogeneously catalyzed reactions, such as the hydrogenation of pyruvate esters on Pd and Pt modified by a cinchona alkaloid [44]. Although the inversion of ee is generally attributed to changes in the reaction mechanism, transformations in the structure of the modifier cannot be discarded [45].

We have also studied the influence of acid solvents as trifluoroacetic acid (TFA, pK_a = 0.3) and acetic acid (pK_a = 4.75), on the enantioselectivity. The addition of a small proportion of TFA (1.70 mmol) to 2-propanol had a strong effect on the selectivity to (*R*)-ethyl lactate, only 5% ee is obtained. A probable explanation of this effect of the TFA is the formation of an ion pair between the protonated modifier and the TFA. This ion pair is the ‘‘real modifier’’ that interacts with the substrate in the enantiodifferentiating step. It seems that under these conditions, the interaction with the substrate is not so efficient, generating a low ee. The extension of the modifier/solvent interaction depends on the acid strength, since the effect is smaller when acetic acid (pK_a = 4.75) is used, which allows to obtain 10% ee (see Table 3).

With respect to the reaction rates, we observed that for the systems modified with (*S*)-(+)-1-aminoindan, the less polar solvents (toluene and *n*-heptane) present the lower activity (Fig. 5b). In the case of toluene, it could be attributed to a possible competence, on the catalyst surface, between solvent and modifier. With respect to *n*-heptane, the result could be explained as function of the low solubility of substrate and modifier in such solvent [39].

Contrary to what happens with cinchonidine, when the system modified with (*S*)-(+)-1-aminoindan was tested in acetic acid and 2-propanol + TFA as solvents, not only the ee was low, but also the reaction rate. Again, this could be due to the fact that when the nitrogen of the $–NH_2$ group is protonated, the configuration acquired by the modifier is unfavorable for an effective interaction with the substrate, thus generating low ee and reaction rates (Table 3 and Fig. 5a and b).

Analyzing Fig. 5a and b, it can be seen that the plots conversion versus time for both modifiers, cinchonidine and (*S*)-(+)-1-aminoindan, present a certain ‘‘flattening’’ for the more polar solvents. These types of curves would indicate a deactivation process, more important in the hydrogenation of ethyl pyruvate when the solvent is acetic acid, since this ‘‘flattening’’ is almost imperceptible in the curves corresponding to *n*-heptane (Fig. 5b) and toluene (Fig. 5a).

4. Conclusions

From the results obtained, it is evident that enantioselective hydrogenations are structure-sensitive reactions, requiring in general, relatively big metallic particles to obtain an efficient enantiodifferentiation. According to this, the Pt/SiO_2 (B) catalyst provides better results.

Among the modifiers used, the (*S*)-(+)-1-aminoindan presented a behavior similar to the one of cinchonidine in the ee% obtained (63%) as well as in the reaction rate in 2-propanol. This was neither the case for the (*S*)-(+)-1-indanol that gave as product a racemic mixture, nor for the (1*R*, 2*S*)-(+)-*cis*-1-amino-2-indanol that showed an effect of ‘‘erosion of enantiomeric excess’’ and a lower reaction rate which is attributed to functional differences between one and the other modifier.

A higher ee% in 2-propanol was obtained when the modifier used was the (*S*)-(+)-1-aminoindan, while in toluene and *n*-heptane the ee% not only decreased considerably, but also the predominant enantiomer was the (*S*)-ethyl lactate. Results in acid medium showed a low performance of the catalytic systems.

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