

Enantioselective Hydrogenation of Ethyl Pyruvate and 1-Phenyl-1,2-propanedione on Catalysts Prepared by Impregnation of Colloidal Platinum on SiO₂

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A hidrogenação enantiosseletiva de piruvato de etila e de 1-fenil-1,2-propanodiona foi estudada a 298 K e sob 40 bar de H₂ sobre um catalisador de platina coloidal estabilizado com cinchonidina (CD) e suportado em sílica. O catalisador foi preparado por impregnação da platina coloidal em sílica, atingindo 1% em massa do metal no suporte. O colóide foi preparado a partir de uma solução aquosa de H₂PtCl₆ estabilizada com diferentes quantidades de CD. O catalisador foi caracterizado por isotermas de adsorção-desorção de N₂ a 77 K e por XPS, XRD e TEM. As reações foram efetuadas em batelada em um reator de aço inoxidável, usando cicloexano como solvente e cinchonidina como modificador quiral. A adição de CD ao catalisador permite a estabilização e o controle do tamanho de partícula da platina, e também afeta o excesso enantiomérico (*ee*) do sistema, levando a um maior rendimento do produto com configuração *R*. A relação entre a concentração de CD adicionada *in situ* e a enantiosseletividade apresenta uma curva do tipo sino nas duas reações estudadas; este comportamento é um indicativo da importância da adsorção competitiva do modificador e do substrato na superfície do catalisador.

The enantioselective hydrogenation of ethyl pyruvate and 1-phenyl-1,2-propanedione was studied at 298 K and 40 bar of H₂ over colloidal Pt stabilized with cinchonidine (CD) and supported on silica. The catalysts were prepared by impregnation of colloidal Pt on SiO₂, leading to a metal load close to 1 wt.%. The colloid was prepared from an aqueous solution of H₂PtCl₆ and stabilized with different quantities of CD. The catalysts were characterized by nitrogen adsorption-desorption isotherms at 77 K, XPS, XRD and TEM techniques. The reactions were carried out in a stainless steel batch reactor using cyclohexane as solvent and cinchonidine as chiral modifier. The addition of CD to the catalysts allows the stabilization and control of the platinum particle size and also affects the enantiomeric excess (*ee*) of the system, affording a higher proportion of the (*R*)-product. The relationship between the enantioselectivity and the CD concentration (added *in situ*) exhibits a bell type curve for both reactions, this being indicative of the importance of a competitive adsorption of the modifier and substrate on the catalyst surface.

Keywords: Pt colloids, enantioselectivity, ethyl pyruvate, 1-phenyl-1,2-propanedione, cinchonidine

Introduction

Enantioselective hydrogenation reactions are important tools to obtain fine chemicals used in pharmaceutical and food products.¹⁻⁴ Thus, the synthesis of chiral compounds is of growing interest; among them, the hydrogenation of α -ketoesters and ketones is the most widely studied.⁵⁻¹⁵ Since Orito *et al.* reported the enantioselective hydrogenation of ethyl pyruvate to (*R*)-ethyl lactate over cinchonidine-modified Pt catalysts

with *ee*'s up to 95%, many other research teams have evaluated the performance of their catalytic systems in this reaction.¹⁶⁻¹⁸ Indeed, this is nowadays a sort of test reaction in the field of asymmetric catalysis. However, when the substrate has more than one centre to be hydrogenated the reaction becomes more difficult, as occurs during the hydrogenation of diones (such as 1-phenyl-1,2-propanedione), both in terms of enantio- and regioselectivity (*RS*).¹⁹⁻²⁶ In this case, the product of interest is (*R*)-1-phenyl-1-hydroxy-2-propanone, which has interesting applications in the synthesis of precursors for hypertension and asthma treatments, among others.²⁷⁻²⁸

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Supported platinum catalysts have been widely studied for this type of application.²⁹ It has been found that metal particle size plays an important role in asymmetric synthesis when performed in the presence of cinchonidine as a chiral inducer. Metal crystals around 3.0 nm obtained with catalysts having metal loading close to 5 wt.% have led to the most promising catalytic behaviour. The catalysts containing lower metal loadings usually display smaller particle sizes and are not appropriate for this purpose. However, using colloid preparation procedures, it is possible to obtain metal particles with different average sizes. In this case, even with low metal loading it is possible to get larger metal crystals. In fact, it is well known that metal colloids with different particle sizes can be prepared by this procedure in the presence of a chiral inducer, which may lead to preferential hydrogenation to (*R*)-ethyl lactate during hydrogenation of ethyl pyruvate.³⁰⁻³⁸

On the other hand, it is also well known that, in different reaction conditions, there may be leaching from nanoparticles.³⁹⁻⁴¹ The leaching mainly occurs in reactions at high temperatures or carried out under extreme conditions, such as C-C coupling, Heck reaction, etc.. Taking into account this important phenomenon, we tried to reduce the leaching problems from our catalysts to a minimum level.⁴² We have employed conditions that decrease this effect, such as the use of nanoparticles on a support that can stabilize the metal clusters or inhibit the release of metal atoms from the particles. Also, in the hydrogenation reactions the solvent used was of low polarity and non oxidant, this to avoid the solvolysis of the metal-oxygen bonds through which the catalyst is attached to the SiO₂.

In this work, supported Pt catalysts were synthesized in which the active phase was first obtained from a colloidal dispersion and then impregnated on the support. Cinchonidine (CD), which is often used as a chiral inducer, was employed as colloid stabilizer because it limits the excessive growth of metal particles. Additionally, CD may induce enantioselectivity towards the desired product. As it is well known, most of the heterogeneous asymmetric hydrogenations are performed at room temperature with addition of the chiral inducer and the substrate at the beginning of the reaction, being this temperature the most appropriate to obtain CD in its open 3 conformation.³⁸ However, at higher temperatures, this inducer exists, in a certain extent, in other conformations. Consequently, in some experiments an additional amount of CD was also provided with the substrate, and considering that in the colloidal synthesis the extent of CD added may not be the appropriate. The modified colloidal platinum was supported on commercial silica and the catalytic activity was studied in two reactions: the hydrogenation of ethyl pyruvate and the hydrogenation of 1-phenyl-1,2-propanedione. Both

reactions were performed at 298 K and 40 bar of H₂ using cyclohexane as solvent in a batch reactor. The catalysts were characterized by powder XRD (X-ray diffractometry), TEM (transmission electron microscopy) and XPS (X-ray photoelectron spectroscopy).

Experimental

Materials

Chloroplatinic acid hydrate, 1-phenyl-1,2-propanedione, ethyl pyruvate, cinchonidine and cyclohexane were supplied by Aldrich, formic acid by Merck and H₂ (99.995%) by AGA. The substrates and solvents were purified by distillation prior to each hydrogenation reaction.

Catalyst preparation

The colloids were prepared from an aqueous solution of H₂PtCl₆·6H₂O under reflux at 373 K with the addition of CD dissolved in 15 mL of an aqueous (0.1 mol L⁻¹) HCOOH solution. After cooling down to room temperature, the colloid was washed with an aqueous solution of NaHCO₃ in order to remove the acidity. The colloidal dispersions were prepared with different quantities of CD, ranging from 2.2 × 10⁻³ to 9.8 × 10⁻³ mol L⁻¹, to give different metal particle sizes. They were labeled as Pt-CD(x)/SiO₂ being x = 2.2 (a), 7.4 (b) and 9.8 (c) mmol L⁻¹ of CD respectively. The catalysts were prepared by impregnation of silica (BASF D-11-11, S_{BET} = 142 m² g⁻¹) with an appropriate amount of the colloidal dispersion to get Pt-loadings of 1.0 wt.%. Chemical analysis performed by atomic absorption spectroscopy revealed that the Pt loading was 0.97 wt.% in the fresh samples, being 0.94 wt.% in the used catalysts.

Characterization

Nitrogen adsorption studies were carried out at 77 K on a Micromeritics ASAP 2010 apparatus. TEM micrographs were obtained with a Jeol Model JEM-1200 EXII System, X-ray diffraction studies were performed with a Rigaku diffractometer and X-ray photoelectron spectra (XPS) were recorded using an Escalab 200R spectrometer provided with a hemispherical analyzer operated in a constant pass energy mode. The Mg K_α X-ray radiation source (hν = 1253.6 eV) was operated at 10 mA and 12 kV.

Hydrogenation reactions

The catalytic behaviour in both reactions, the hydrogenation of ethyl pyruvate and 1-phenyl-1,2-

propanedione, was studied at 298 K and 40 bar of H₂ with cyclohexane as solvent in a stainless steel batch reactor. In reactions that included *in situ* addition of CD, the amount added at the beginning of the reaction led to an initial concentration of 2×10^{-4} mol L⁻¹. The analysis of reactants and products was carried out with a Shimadzu GCMS-QP5050 equipment, using a chiral β -dex 225, 30 m column (SUPELCO) and helium as carrier gas.

Results and Discussion

Characterization of catalysts

X-ray diffraction patterns of the prepared catalysts closely correspond with that displayed by the amorphous silica support. Only a small and wide peak at 2θ ca. 40° corresponding to Pt(110) was observed in the Pt-CD(a)/SiO₂ catalyst. This is a clear indication of the high dispersion of the Pt colloid deposited on the support surface. The absence of diffraction lines due to Pt in the X-ray diffractograms of the other catalysts (b and c) can be attributed to the low Pt content and the small particle size, lower than the limit of detection of this technique (usually around 4 nm).

Metal particle sizes of both colloidal platinum and Pt-CD/SiO₂ catalysts were evaluated by TEM analysis. Particle size measurements showed a very narrow particle size distribution. Table 1 compiles the average values obtained for each colloid, as well as the metal particle size once the impregnation on the support took place. It can be seen that, in both series, the particle size decreases as the CD concentration used in the synthesis increases. This behaviour can be attributed to the stabilizer role of CD, which inhibits the growth of Pt crystallites formed during the reduction of the precursors. This happens because of the interactions between the partially filled “d” orbitals of the metal and the aromatic ring of the quinoline, the quinuclidinic nitrogen and the oxygen of the stereogenic CD center. Similar results have been reported previously by Bönemann.³¹⁻³⁴ Only small changes in the particle size were detected by comparing the colloid dispersion and the corresponding catalysts, confirming the stability of the obtained metal dispersion.

The metal dispersion, estimated from the particle size values assuming a cubic shape for the metallic crystallites, is also given. The results confirm that the used procedure allows an appropriate control of the dispersion or metal particle size. However, if the concentration of CD is lower than 5×10^{-4} mol L⁻¹, the metal particles are much larger and the dispersion becomes unstable.

Microscopy studies included TEM micrographs obtained for fresh and used catalysts, which were analyzed

Table 1. Metal particle sizes determined for the colloidal Pt and Pt-CD(x)/SiO₂ catalysts

Catalyst	CD concentration (mol L ⁻¹)	Particle size (nm)		Dispersion	ee*
		Pt colloidal	1 wt.% Pt-CD(x)/SiO ₂		
(a)	0.0022	3.7	3.4	0.25	23
(b)	0.0074	2.5	2.4	0.35	27
(c)	0.0098	1.7	1.6	0.53	34

Where x corresponds to (a), (b) and (c). * Enantiomeric excess average for (*R*)-ethyl lactate obtained on 1wt.% Pt-CD(x)/SiO₂ prepared in the presence of different CD concentrations.

to verify the possibility of leaching of the supported nanoparticles. We have found no changes in the Pt nanoparticles size, except in non-supported colloids, in which sinterization of the nanoparticles was detected. Additionally, chemical analysis by atomic absorption spectroscopy did not show significant changes in the Pt contents of fresh and used catalysts.

Other simple qualitative test performed to analyze the possibility of leaching was to treat the catalyst with THF (a solvent in which the nanoparticles are suspended), followed by filtering of the solid phase. The filtrate was a colorless solution, which roughly indicates that the nanoparticles did not undergo leaching from the support.

The latest research suggests that the only way to verify this phenomenon is the use of special membrane reactors. These membranes have pore diameters smaller than the clusters, and will only allow the passage of atoms (or other chemical species with very small diameters), allowing their separation and quantification. In subsequent works we intend to study some reactions in membrane reactors to verify this behavior at the atomic level.

XPS studies were performed after *in situ* treatment of the catalysts with hydrogen at room temperature to remove possible surface oxidation. A binding energy of 314.9 eV was found for the Pt 4d_{5/2} core-level, indicating the presence of Pt in a reduced state (Pt⁰). Indeed, this result can be taken as indicative of the efficiency of the reduction procedure employed in this work, which consists in the decomposition of formic acid in aqueous solution at temperatures close to 80 °C, producing H₂ gas to reduce platinum ions to metal particles. Additionally, it should be mentioned that N 1s core-level spectra showed the presence of two types of nitrogen, centered at 398.0 ± 0.1 and ca. 400 ± 0.1 eV, in line with the two different surroundings of nitrogen in the quinolinic and quinuclidinic ring, respectively. As expected, the proportion of both nitrogen atoms is close to 1 in the three catalysts (see Figure 1).

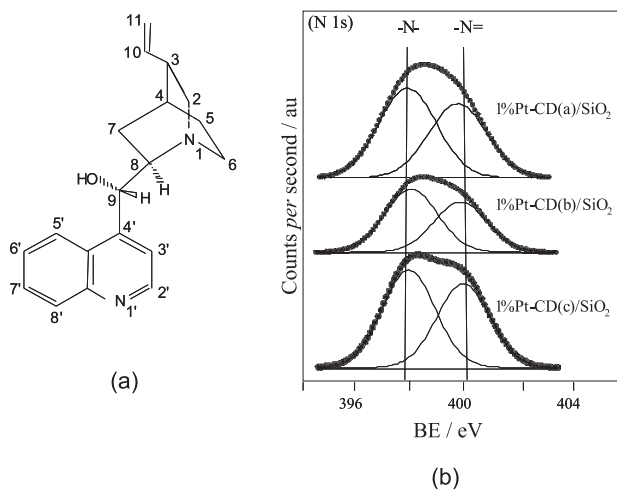


Figure 1. (a) Cinchona alkaloid with the two types of nitrogen atoms (N_1 and $N_{1'}$) detected by XPS. (b) XPS core level spectra of N1s for the studied catalysts.

Table 2 compiles the Pt/Si and N/Si atomic surface ratios. It can be seen that, as the CD concentration used in the synthesis increases, both the Pt/Si and the N/Si atomic surface ratios also increase. This behaviour is explained by the stabilizing role played by the CD molecule during the synthesis. Thus, as the CD concentration increases, the formed metal crystallites do not have the possibility to grow, leading therefore to smaller metal particle sizes. Consequently, a higher amount of exposed Pt atoms should be expected. Additionally, once these aggregates were stabilized with CD molecules, which contain nitrogen atoms, the N/Si atomic surface ratio should also increase.

Table 2. Pt/Si and N/Si atomic surface ratios for the 1wt.% Pt-CD/SiO₂ catalyst

Catalyst	[CD] mol L ⁻¹	Pt/Si	N/Si
(a)	0.0022	0.0010	0.008
(b)	0.0074	0.0058	0.026
(c)	0.0098	0.0193	0.033

Catalytic activity

Hydrogenation of ethyl pyruvate

Figure 2 shows a scheme of the hydrogenation of ethyl pyruvate (EP). It has been demonstrated that, using cinchonidine chiral alkaloid, it is possible to induce a preferential formation of (*R*)-lactate.⁴³⁻⁴⁴ In the present study the enantioselective hydrogenation of ethyl pyruvate was carried out in liquid phase at 298 K and 40 bar overall pressure on colloidal platinum and on Pt-CD/SiO₂ catalysts obtained by impregnation of the colloids on the support. Experimental variables such as the weight of the catalysts

and the concentration of CD added with the substrate during the reaction were also studied. The hydrogenation of EP was carried out initially in the presence of 2 mg of colloidal Pt. Activity results showed very low conversion level even after long reaction times. Thus, at 250 min the conversion values reached 11% for the catalyst with smaller particle size, and 9 and 7% for those with larger metal particles respectively. Regarding enantioselectivity, only a slight *ee* for the (*R*)-ethyl lactate was found. The reaction performed with the catalyst with smaller particle size showed an *ee* value of 15%, being even lower for the catalysts displaying higher particle sizes. It should be mentioned that the evolution of the conversion level with time for the three studied catalysts reached almost constant level after about 60 min. Deactivation by sintering of the metal phase is responsible for the observed behaviour, which may occur under these mild experimental conditions in colloids but is not likely to occur with supported metal catalysts. Poisoning of the metal sites by traces of compounds present in the substrate solution has been also suggested as responsible for the deactivation. Nevertheless, in our experiments, the reactants were purified by distillation prior to the catalytic studies. Blank experiments performed in absence of catalysts did not show any conversion even after 400 min.

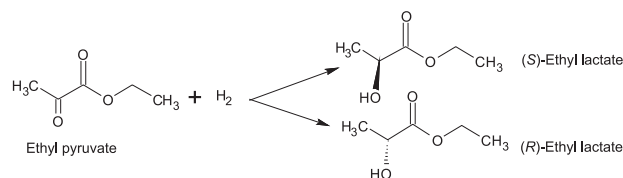


Figure 2. Hydrogenation of ethyl pyruvate.

Similar studies were carried out with the Pt-CD/SiO₂ catalysts. Starting from the solids with the smallest metal particle size, the effect of the weight of catalysts was studied in the hydrogenation of EP (0.02 mol L⁻¹) at 298 K and 40 bar of H₂. The results showed a linear increase in the conversion level during the first 5 min of reaction and then the reaction rates decrease, reaching an almost complete conversion after two hours. There are significant differences in the conversion levels depending on the catalyst weight.

Under the same experimental conditions (0.02 mol L⁻¹ solution of EP, 100 mg of catalyst, 298 K and 40 bar of H₂), the three catalysts were tested. The time course of conversion is similar to that displayed by the colloids, although conversions are much higher than that exhibited by them. The trend was the same: the highest the CD concentration during the colloid synthesis, the highest the activity obtained. Thus, at the same reaction time, *i.e.* 250 min, the conversion level increases from 80 to 99% when decreasing the size of the Pt crystallites. With

regard to the enantioselectivity, it is also affected by the characteristics of the metal clusters. Again, the *ee* depends on the metal particle size, being higher the *ee* for the (*R*)-ethyl lactate in the catalysts with lower particle size.

Table 1 shows the *ee* values for the catalysts prepared by the colloidal route in the presence of different chiral modifier concentrations. The catalytic behaviour of a non modified Pt/SiO₂ (prepared by impregnation of H₂PtCl₆ on silica followed by calcination and reduction) in the hydrogenation of EP leads to the racemic mixture, confirming that the chiral modifier is essential to induce chirality. It has been demonstrated in previous studies that metal particle size in Pt catalysts employed in asymmetric hydrogenation controls the enantioselectivity of the reaction. It has been found that, for a given CD concentration, metal particle sizes in the range of 3-4 nm show the maximum enantiomeric excess. This behaviour was explained on the basis of adsorption of CD on the active sites. Planar adsorption of the modifier on crystal faces is favoured when crystal dimensions are in the range of 3-4 nm, and this adsorption mode is the most appropriate to generate the open 3 conformers which are responsible for the formation of the (*R*)-enantiomer. On the other hand, planar adsorption of CD is limited on Pt particles smaller than 3 nm.⁵

The results of the present work show the opposite trend. This particular behaviour can be due to the different approach chosen to prepare the catalysts. As they were prepared in the presence of CD, it is likely that an important quantity of the modifier remained linked to the Pt surface atoms, being highest the amount of CD bonded to the smaller crystals. Therefore, the higher *ee* values can be related to the higher CD concentration instead of particle size. It is well known that the concentration of added modifier during the catalytic reaction plays an important role in both activity and enantioselectivity in this kind of reactions. For this reason, the effect of addition of CD with the substrate at the beginning of the reaction was also studied. Figure 3 shows the results obtained for the three catalysts. A typical bell type curve was found with each catalyst. The observed behaviour confirms that an optimum amount of CD is required to induce chirality. The *ee* displayed in the experiments without the addition of CD, in the range of 23 to 34% for the different catalysts, is attributed to the CD linked to the metal during the synthesis. As can be seen in Figure 3, the amount of CD is not optimized to give a maximum *ee*, which depends on the metal particle size. At lower CD concentration, the Pt surface coverage is rather limited and consequently leads to lower values. As the CD concentration increases, also the enantioselectivity increases, up to reaching maximum *ee*. At higher CD concentration, flat adsorption of CD moieties on the metal surface is highly inhibited, being also possible

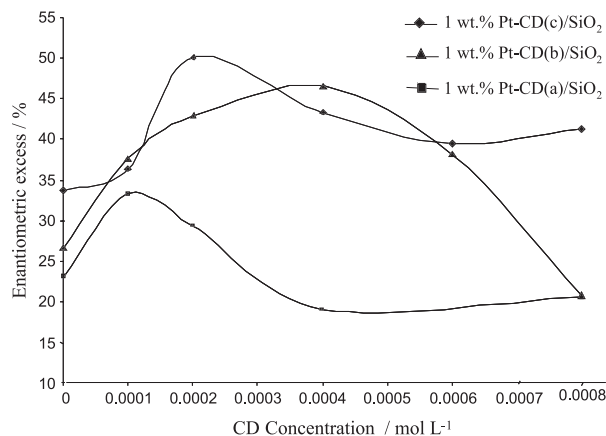


Figure 3. Effect of the CD concentration during the EP hydrogenation (298 K, 40 bar of H₂, 1 wt.% Pt-CD/SiO₂ catalyst) on the *ee* of (*R*)-ethyl lactate.

the formation of CD dimers, (CD)₂.⁴⁵ Both facts made more difficult to induce the desired chirality.

Table 3 summarizes data on the pseudo first order reaction rates for EP hydrogenation determined in the presence of the studied catalysts at different CD concentrations added *in situ*. Experimental values up to 60 min were considered. It can be observed that an increase in CD values produces a decrease in the rate constants whatever the catalyst. Additionally, the values of the rate constants increase in parallel with the metal particle size. The exception is the catalyst with higher particle size, because at higher CD concentration the rate constant also decreases, but the enantioselectivity is favoured. Table 4 summarizes the conversion level, *ee* values and the yield of (*R*)-ethyl lactate for the different catalysts under the experimental conditions employed in this work. Figure 4 displays the evolution of the concentrations of substrate and products during the reaction, for the catalysts with the highest metal particle size in the presence of CD added at the beginning of the reaction. It can be seen that the decrease in CD concentration follows a pseudo first order reaction kinetics and the products appear as a consequence of parallel reactions, being favoured the formation of (*R*)-ethyl lactate. Under the conditions tested, the reaction is complete after 150 min.

Hydrogenation of 1-Phenyl-1,2-propanedione on 1wt.% Pt-CD/SiO₂

Figure 5 shows a scheme of the enantioselective hydrogenation of 1-phenyl-1,2-propanedione. The reaction was studied at 298 K and 40 bar of H₂ using the catalyst 1wt.% Pt-CD(c)/SiO₂. It was found that, using this system, it is possible to induce the preferential formation of (*R*)-1-phenyl-1-hydroxy-2-propanone.

Under the conditions employed, the main products were the regioisomers (*R*)- and (*S*)-1-hydroxy-1-phenylpropanone

Table 3. Pseudo first order reaction rate constants for the hydrogenation of EP at 298 K and 40 bar of H₂ on 1wt.% Pt-CD/SiO₂ at different CD concentrations

CD (mol L ⁻¹)	*k (min ⁻¹)		
	1wt.% Pt-CD(a)/SiO ₂	1 wt.% Pt-CD(b)/SiO ₂	1wt.% Pt-CD(c)/SiO ₂
0	0.0035	0.0362	0.0269
1.0E-04	0.0105	0.0236	0.0209
2.0E-04	0.0074	0.0226	0.0111
4.0E-04	0.0050	0.0086	0.0095
6.0E-04	0.0149	0.0081	0.0067
8.0E-04	0.0149	0.0065	0.0063

*calculated up to 60 min of reaction.

Table 4. Conversion, enantiomeric excess and yield of (*R*)-ethyl lactate in the ethyl pyruvate hydrogenation at 250 min

Catalyst	Conversion (%)	ee (%)	Yield of (<i>R</i>)-ethyl lactate (%)
1wt.% Pt-CD(a)/SiO ₂	97	23 ¹	60
1wt.% Pt-CD(b)/SiO ₂	100	27 ¹	63
1wt.% Pt-CD(c)/SiO ₂	100	34 ¹	67
1wt.% Pt-CD(c)/SiO ₂	100	50 ²	76

¹ Conditions: 40 bar, 298 K, 0.02 mol L⁻¹ of EP in cyclohexane and 100 mg of 1wt.% Pt-CD/SiO₂. ² Under the same conditions as in ⁽¹⁾ but with optimum concentration of CD: 2 x 10⁻⁴ mol L⁻¹ added *in situ*.

and (*R*)- and (*S*)-2-hydroxy-1-phenylpropanone. No over-hydrogenated products (diols F, G, H, I in Figure 5) were observed. In all catalytic tests the regioselectivity, defined as $rs = [B] + [C] / [D] + [E]$ (B, C, D and E in Figure 5), was lower than 5%. This behaviour may be explained in terms of electronic effects, because the aromatic ring contributes to polarize the C=O bond close to the ring to a higher extent, and therefore the reactions leading to (*R*)-1-phenyl-1-keto-2-propanol and (*S*)-1-phenyl-1-keto-2-propanol are less favoured. Figure 6 shows the evolution of substrate and products concentrations with time during the hydrogenation of 1-phenyl-1,2-propanedione on one representative catalyst, at 298 K, 40 bar of H₂ and 100 mg of 1wt.% Pt-CD(c)/SiO₂. The results indicate that, under these experimental conditions, the catalyst is highly active with conversion close to 90% after 420 min, but with lower *ee* and *R/S*. Considering the previous results obtained in EP hydrogenation, it would be possible to enhance the yield of the desired products by adjusting CD coverage. For that reason, the effect of the CD concentration added at the beginning of the reaction was studied. The evolution of the conversion with time showed significant differences depending on the CD concentration. The curves follow

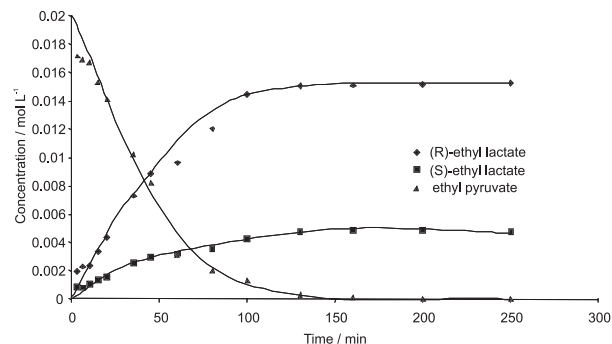


Figure 4. Evolution of substrate and products concentrations during the EP hydrogenation at 298 K and 40 bar of H₂ on the 1wt.% Pt-CD(c)/SiO₂ catalyst.

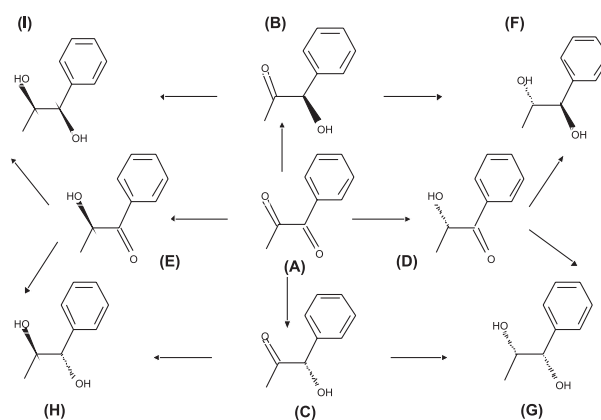


Figure 5. Reaction scheme of the hydrogenation of (A) 1-phenyl-1,2-propanedione. (B) (*R*)-1-phenyl-1-hydroxy-2-propanone; (C) (*S*)-1-phenyl-1-hydroxy-2-propanone; (D) (*S*)-1-phenyl-1-keto-2-propanol; (E) (*R*)-1-phenyl-1-keto-2-propanol; (F) (1*R*,2*S*)-1-phenyl-1,2-propanediol; (G) (1*S*,2*S*)-1-phenyl-1,2-propanediol; (H) (1*S*,2*R*)-1-phenyl-1,2-propanediol; (I) (1*R*,2*R*)-1-phenyl-1,2-propanediol.

the trends already shown and approach first order reaction kinetics. A summary of the first order reaction data obtained for the 1wt.% Pt-CD(c)/SiO₂ catalyst under the experimental conditions employed in this work is given in Table 5. An increase in the rate constant upon increasing CD concentration is observed. When the reaction is performed in absence of additional amount of CD, the reaction takes place but at a lower reaction rate. The enantioselectivity also shows important changes with CD concentration. Therefore, the CD contributes to the generation of modified catalytic sites which are enantioselective and more active than the metal sites.

Figure 7 shows the effect of CD concentration on the enantiomeric excess of (*R*)-1-phenyl-1-hydroxy-2-propanone. Trends similar to those previously reported can be observed: a bell-type plot with the maximum corresponding to an *ee* value of 42% was found. This behaviour can be explained on the basis of surface coverage as discussed previously. The fact that *ee* values

Table 5. Pseudo first order reaction rate constants as a function of CD concentration for the 1-phenyl-1,2-propanedione hydrogenation on 1wt.% Pt-CD(c)/SiO₂ catalyst

CD (mol L ⁻¹)	Reaction rate constant (min ⁻¹)
0	0.0008
1.0E-04	0.0014
2.0E-04	0.0016
4.0E-04	0.0020
6.0E-04	0.0026
8.0E-04	0.0028

Conditions: T = 298 K, P_{H₂} = 40 bar, 100 mg of 1wt.% Pt-CD(c)/SiO₂, solvent = cyclohexane.

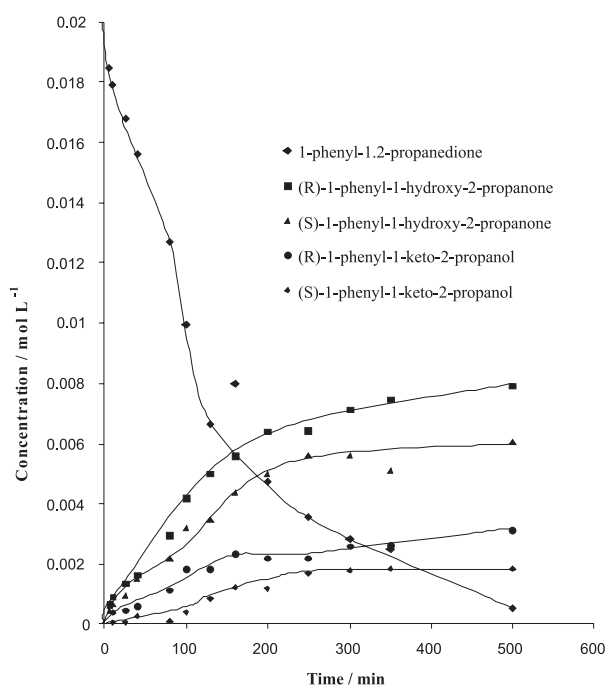


Figure 6. Evolution of reactant and products concentrations during the hydrogenation of 1-phenyl-1,2-propanedione at 298 K and 40 bar of H₂, with 100 mg of 1wt.% Pt-CD(c)/SiO₂ catalyst.

are much lower than those observed for the same catalyst in the ethyl pyruvate hydrogenation (under similar reaction conditions) can be understood by comparing the nature of the substrate. The adsorption properties of both molecules on the metal centers are different; the adsorption of the dione is stronger as a consequence of the aromatic ring. Therefore, the adsorption of the 1-phenyl-1,2-propanedione on the non-modified sites is stronger than that for EP and consequently the enantioselectivity is lower. Even though the obtained *ee* values are rather low, confirming the difficulties to induce chirality in this reaction, they are not too far from the best reported values for enantioselectivity in the same system.¹⁹⁻²⁶

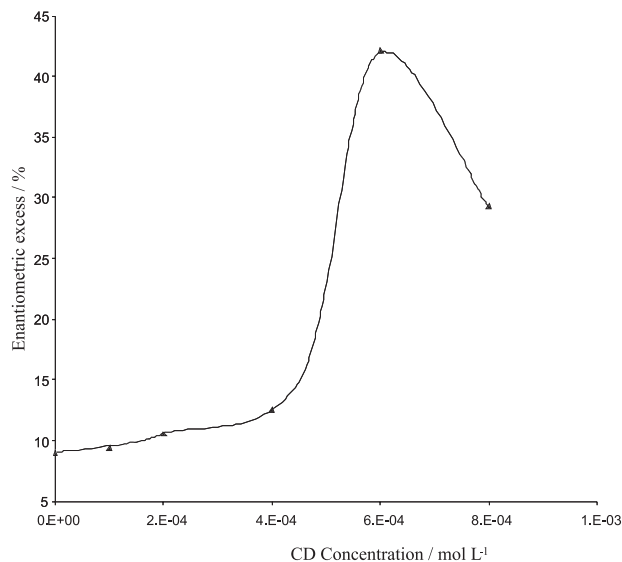


Figure 7. Effect of CD concentration on the enantiomeric excess of (*R*)-1-phenyl-1-hydroxy-2-propanone during the hydrogenation of 1-phenyl-1,2-propanedione on 1wt.% Pt-CD(c)/SiO₂ at 298 K and 40 bar of H₂.

Conclusions

The results presented here show that it is possible to prepare chiral metal supported catalysts when the metallic component is formed from a metal dispersion in the presence of the chiral modifier as stabilizer. The amount of modifier strongly affects both the particle size and the catalytic behaviour. Higher activity and better enantioselectivity were observed for the catalyst with smaller metal particle size in the EP hydrogenation. The addition of CD during the catalytic reaction contributes to improve the behaviour. The optimum amount of CD required depends on the nature of the catalysts and the *ee* exhibits a bell-type dependence on CD concentration. Similar trends were obtained in the hydrogenation of the dione, although a lower enantiomeric excess was obtained. This behaviour was explained in terms of the differences in the adsorption of both substrates on the metal sites.

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