

ENANTIOSELECTIVE HYDROGENATION OF 1-PHENYL-1,2-PROPANODIONE ON Pt/ZrO₂ CATALYSTS

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ABSTRACT

The enantioselective hydrogenation of 1-phenyl-1,2-propanedione at 298K and pressure of 40 bar of H₂ over zirconia supported Pt catalysts has been studied. Three different zirconia were prepared: i) ZrO₂-P obtained by a precipitation procedure from ZrOCl₂, ii) MSZrO₂ obtained by a sol-gel procedure using cetyltrimethylammonium bromide (CTMABR) as surfactant to get a mesostructured solid iii) CNTsZrO₂ obtained after impregnation of carbon nanotubes with ZrO(NO₃)₂ followed by pyrolysis and calcination. Pt (1wt%) was introduced on the support by impregnation of an aqueous solution of H₂PtCl₆. The catalysts were characterized by nitrogen adsorption-desorption isotherms at 77 K, hydrogen chemisorption, 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 presence of CD in the reaction medium is necessary to induce an enantiomeric excess (ee) of the desired product R-1-phenyl-1-hydroxy-2-propanone. In all the studied systems, the relation between the enantioselectivity and the CD concentration added *in situ* exhibits a bell type curve; indicative of the importance of competitive adsorption between the modifier and the substrate on the catalyst surface. On the other hand, confinement effect led to an important enhancement in the activity in those catalysts supported on mesostructured supports, mainly in the Pt/CNTsZrO₂ catalyst.

Keywords: Platinum, mesostructured supports, enantioselective hydrogenation.

INTRODUCTION

Heterogeneous enantioselective hydrogenation of diketones on cinchona alkaloid modified platinum represents a promising route for the synthesis of chiral molecules with high optical purity [1-3]. As catalysts Pt, Pd and Ir supported on SiO₂, Al₂O₃, among others are used [4-8]. 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 their catalytic systems in the mentioned reaction [9-11]. Indeed, this reaction 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 as 1-phenyl-1,2-propanedione both in terms of enantio- and regioselectivity (rs)[12-19]. In the latter, the product of interest is (*R*)-1-phenyl-1-hydroxy-2-propanone, which has interesting application in the synthesis of compounds used as precursors for hypertension and asthma treatments, among others[20-21].

Supported platinum catalysts have been widely studied for this type of applications [22]. 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, they are not appropriate for this purpose.

The selection of the support has been relevant in the preparation of heterogeneous catalysts for the hydrogenation enantioselective of α -ketoesters, α -functionalized ketones and α , β -diketones[23]. Several groups have tried to improve the hydrogenation of ethyl pyruvate by preparing cinchonidine-modified Pt catalysts on various supports. Thus, Hall et al.[24] described the use of a Pt/MCM-41 catalyst which exhibits low reaction rate due to mass transfer limitation and enantiomeric excess up to 64%. Zeolites of different structures and acidities can also display high enantioselective hydrogenation on supported on Pt catalysts. In fact, Böhmer et al.[25] have reported the re-use of Pt/HNaY zeolite in the hydrogenation of ethyl pyruvate in acetic acid and cyclohexane reaching an important e.e. (88%). Additionally, e.e. up to 75% were reported for Pt/clay catalysts (28% e.e. for Rh/K-10)[26], while e.e. below 35% were described for Pt/C catalysts despite improvement by oxidative treatment [27]. Nevertheless, two commercially available 5% Pt/Al₂O₃ catalysts have emerged as "standard" catalysts: E4759f from Engelhard and JMC 94 from Johnson Matthey [28]. In the last few years, researches have been focused in improving the structural and morphological properties of the support to enhance the catalytic behavior. Creating successful mesoporous silicates enantioselective catalysts remains as an important goal for the chemicals and pharmaceuticals industries, with considerable attention being focused on chirally modified metals as promising candidates. These materials in silicate

form have potential applications in catalysis for their use as enantioselective catalysts for asymmetric catalysis. One of the main advantages of these structured solids compared to the traditional supports is that it can produce a confinement effect which can favourably affect both the activity and the selectivity in different reactions.

Thus, the use of Pt on mesoporous MCM-41 in the enantioselective hydrogenation of 1-phenyl-1,2-propanedione was successfully demonstrated. Toukoniitty et al. [29] have studied three different metal contents (5, 10 and 15 wt.%) of Pt on MCM-41 modified with (-)-cinchonidine (CD), obtaining a maximum enantiomeric excess of (*R*)-1-phenyl-1-hydroxy-2-propanone close to 44% using the 15 wt.% Pt/MCM-41 catalyst. This behaviour was attributed to the larger metal Pt particles displayed by this catalyst. Similar results in terms of activity and enantioselectivity were obtained by Reyes et al. [30] in the same reaction using a 1 wt. % Pt/MCM-41. The observed behaviour has been attributed to confinement effects produced into the hexagonal channel of the MCM-41.

Sol-gel technique has been used in some studies in the synthesis of Si and Ti nanotubes. This kind of systems have attracted the attention due to their important applications, because of their excellent properties and technological characteristics such as thermal and chemical stabilities, low electrical conductivities and high degree of biocompatibility [31-32]. Thus, ZrO₂ has showed important properties from the catalytic point of view and also ZrO₂ films on a metal surface have been extensively used as a protection agent against corrosion [33-34]. ZrO₂ mesostructured has been prepared from a surfactant, such as cetyltrimethylammonium bromide (CTMABr), which acts as template of nanotubes with a given diameter of channel [35]. Gels of oxides in the presence of a surfactant or appropriate templates produce nanotubes. They also may be obtained by covering of carbon nanotubes with gels of the oxides followed by calcination [36]. These solids display high surface areas being materials with potential catalytic applications [33].

The aim of the present work is to obtain and evaluate new series of Pt catalysts supported in mesostructured ZrO₂ solids of MCM-41 type as an alternative to the classic catalyst for the enantioselective hydrogenation of 1-phenyl-1,2-propanedione using cinchonidine (CD) as modifier (Fig. 1). The effect of the method used to obtain the support, which strongly affects the morphologic characteristics as well as the concentration of the chiral modifier on the catalytic behaviour of the solids is studied.

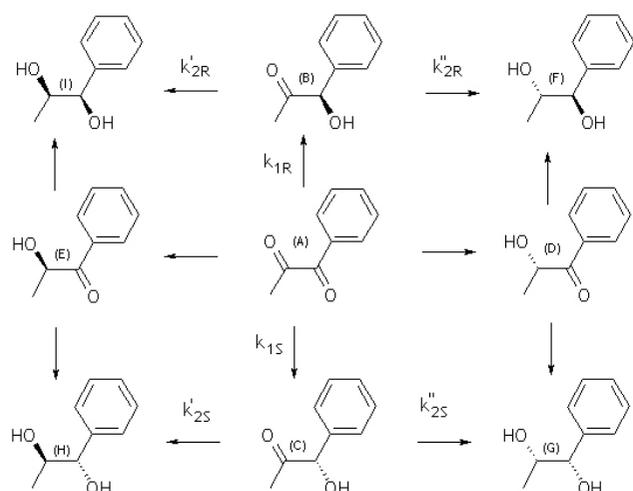


Figure 1 Reaction scheme of the hydrogenation of (A) 1-phenyl-1,2-propanedione; (B) (R)-1-hydroxy-1-phenyl-2-propanone; (C) (S)-1-hydroxy-1-phenyl-2-propanone; (D) (S)-2-hydroxy-1-phenyl-1-propanone; (E) (R)-2-hydroxy-1-phenyl-1-propanone; (F) (1R,2S)-1-phenyl-1,2-propanediol; (G) (1S,2S)-1-phenyl-1,2-propanediol;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

EXPERIMENTAL

Supports preparation.

Precipitated ZrO_2 (ZrO_2 -P).

ZrO_2 was obtained by precipitation of $ZrOCl_2$ with ammonia solution using a procedure already described [37]. The solid was dried with bidistilled H_2O to constant conductivity. The solid was dried at $120^\circ C$ during 8 h and calcined at $550^\circ C$ for 2 h.

Mesostructured ZrO_2 ($MSZrO_2$).

Cetyltrimethylammonium bromide (CTMABr) was dissolved in water under continuous stirring at $40^\circ C$ to obtain a clear micellar solution [38]. Then zirconyl chloride was added to the solution and the pH value of the gel was adjusted with sodium solution (1.4 mol L^{-1}) to 11.5 in order to induce around the formed micelles the hydrolysis and the polycondensation of the inorganic precursor. After stirring for several minutes with the molar composition of $1:0.10:102 = \text{CTMABr} : ZrOCl_2 \cdot 8H_2O : H_2O$ was sealed in a teflon autoclave. The hydrothermal treatment was at $60^\circ C$ for 24 h. The template was removed by solvent extraction (using ethanol), during 30 h. Later on, the solid was calcined in nitrogen flow 3 h at $540^\circ C$ and then in air flow at $540^\circ C$ for 8 h to removed the remaining organic matter.

Impregnation of carbon nanotubes ($CNTsZrO_2$).

Carbon nanotubes were prepared following a procedure already reported [39].

0.3000 g of carbon nanotubes were mixed with 20 mL of a 0.5 mol L^{-1} of a $ZrO(NO_3)_3$ solution. This suspension was kept under ultrasonic vibrations for 10 min and then under boiling conditions for 3 h to evaporate the solvent. The final solid was calcined in Ar at $600^\circ C$ for 2 h. A grey powder was obtained which was then calcined in air at $600^\circ C$ for 2 h to remove the CNTs leading to a white powder.

Catalysts preparation

ZrO_2 , $MSZrO_2$, $CNTsZrO_2$ supports above described and an aqueous solution of chloroplatinic acid containing the amount of Pt precursor necessary to get catalysts containing 1 wt% of Pt were placed in a rotaevaporator under stirring at $35^\circ C$ for 1h. Then the solvent was removed by evacuation at the same temperature. The obtained solids were calcined in air at $300^\circ C$ for 2 h and reduced in hydrogen flow of 100 mL/min at $500^\circ C$ for 2h. The obtained catalysts were labeled as $1\text{wt}\%Pt/ZrO_2$, $1\text{wt}\%Pt/MSZrO_2$ and $1\text{wt}\%Pt/CNTsZrO_2$.

Characterization

Nitrogen adsorption at 77K was carried out in a Micromeritics ASAP 2010

apparatus. TEM micrographs were obtained in a Jeol Model JEM-1200 EXII System, X-ray diffraction studies were performed in a Rigaku diffractometer.

Hydrogenation reaction

The hydrogenation of 1-phenyl-1,2-propanedione, was studied at 298 K and 40 bar of H_2 with 0.01 mol L^{-1} of substrate, 100 mg of catalysts and cyclohexane as solvent in a stainless steel batch reactor. In reactions that include addition of the CD *in situ* the concentration 0.1 to 1.0 mol L^{-1} was added at the beginning of the reaction. The analysis of reactants and products was followed by a GC-MS device (Shimadzu GCMS-QP5050), using a chiral β -dex 225, 30 m column (SUPELCO) and helium as carrier gas.

RESULTS AND DISCUSSION

Figure 2 display the X-ray diffraction pattern of the prepared supports. ZrO_2 prepared by precipitation of $ZrOCl_2$ shows the characteristic reflexions due to monoclinic and tetragonal phases whereas no low angle XRD reflexions were observed for the nanostructured ZrO_2 neither to that prepared by impregnation of carbon nanotubes. Similar fact was found by Larsen et al [40] and Blin et. Al [38] describing the synthesis of sulfated mesoporous zirconia mediated by lauryl sulfate in alkaline solution and CTMABr respectively. The authors suggest that in contrary to the synthesis of silica mesoporous structured materials, the pore formation mechanism does not imply bi or three dimensional X-ray detectable ordering. Indeed, even if low angle signal is not observed in the XRD-pattern, samples exhibit a uniform pore size distribution in the range of mesoporous. In the present study, in agreement with Blin [38] the absence of small angle reflexion line can be attributed to a relative large pore size distribution. The textural characteristic of zirconia will be discussed below.

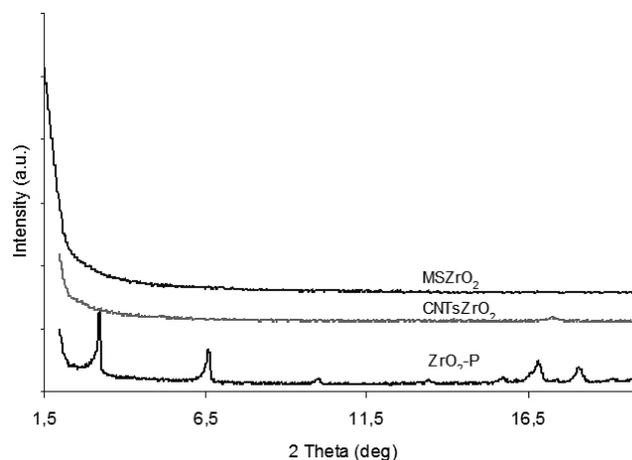


Figure 2. XRD patterns of ZrO_2 supports.

Table 1. Surface area and pore volume of the prepared ZrO_2 supports

Support	S_{BET} , $m^2 g^{-1}$	Pore volume, $cc g^{-1}$
$MSZrO_2$	95	0.18
$CNTsZrO_2$	87	0.18
ZrO_2 -P	101	0.13

Figure 3 shows the nitrogen adsorption isotherms of the studied supports. The isotherms correspond to type IV in the classification of BDDT [39]. The adsorption branch of the isotherm can be decomposed in three parts: the monolayer-multiple adsorption of nitrogen, the capillary condensation of nitrogen within the mesopores and then the saturation. The differences in the hysteresis loops reveal the presence of open capillaries characteristic of MCM-41 kind of materials for $MSZrO_2$ and $CNTsZrO_2$ however, in the former the pore size distribution is narrower. The ZrO_2 -P displays a hysteresis loop indicative of transitional ink bottle pores. Table 1 compiles surface area and pore volumes of the prepared supports. All ZrO_2 samples display a surface area close to $100 \text{ m}^2 g^{-1}$ and pore size in the range of mesopores. The ZrO_2 exhibits a wider pore size distribution in the range of 2.5 to 20 nm, whereas in the $MSZrO_2$ and $CNTsZrO_2$ supports, the pores distribution is narrower and exhibit an important fraction close to 2.0 to 4.0 nm.

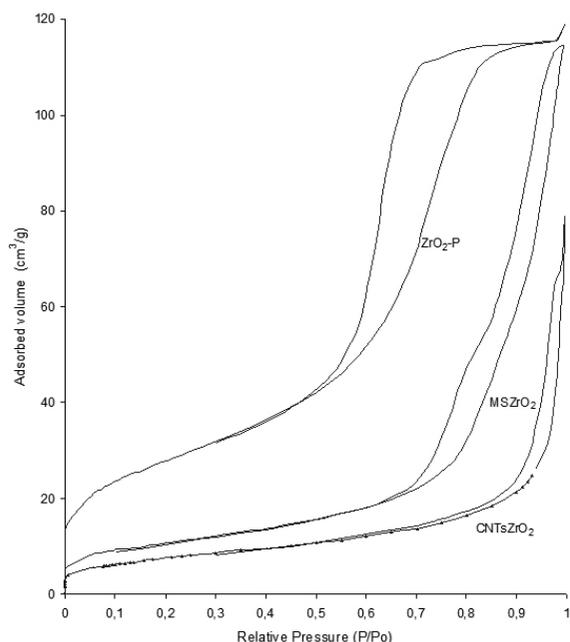


Figure 3. Nitrogen adsorption-desorption isotherms at 77 K on ZrO₂ supports.

Table 2 summarizes the average particle sizes obtained from TEM results and the estimated metal dispersion. As can be seen, the results show that platinum display good dispersion levels and the obtained particle size values are in the range 2.4 to 4.0 nm. The smallest average metal crystals was displayed by Pt catalysts supported on CNTsZrO₂ in which is likely that the metallic species can be located into the channel of the support and the grow of the Pt crystals as consequence of calcinations and reduction treatments is highly restricted. Conversely, the highest average metal particle was exhibited by the Pt/ZrO₂-P catalyst, in which the support possesses a broader pore size distribution and the metallic crystals are deposited on open mesopores.

Table 2. Platinum particle size (d) obtained by TEM and metal dispersion (D) evaluated from chemisorption results of Pt/ZrO₂ catalysts

Catalysts	d _{TEM} , nm	D _{CHEM}
1%Pt/MSZrO ₂	3.2	0.51
1%Pt/CNTsZrO ₂	2.4	0.58
1%Pt/ZrO ₂ -P	4.0	0.41

TEM micrograph of the calcined ZrO₂ materials, show for the Pt/MSZrO₂ and Pt/CNTsZrO₂ samples, typical shapes of nanostructured solids with a regular hexagonal array of mesoporous channels, in good agreement with those previously reported by Beck et al. [41] as can be seen in Figure 4. However, it is convenient to mention that studying TEM micrographs of the former catalyst, it was also found areas in which amorphous support was detected. The presence of Pt crystals located inside the channel of structured supports can be clearly observed, being the metal crystal size rather uniform for these samples, showing values comparable with the pore size of these supports. With regard to the Pt/ZrO₂-P catalysts, it exhibits a broader metal particle size distribution, in the range of 1.5 to 8.0 nm being the average of 4.0, higher than those found by the metal supported on the structured carriers. A summary of the average Pt particle size in the studied catalysts is given in Table 2.

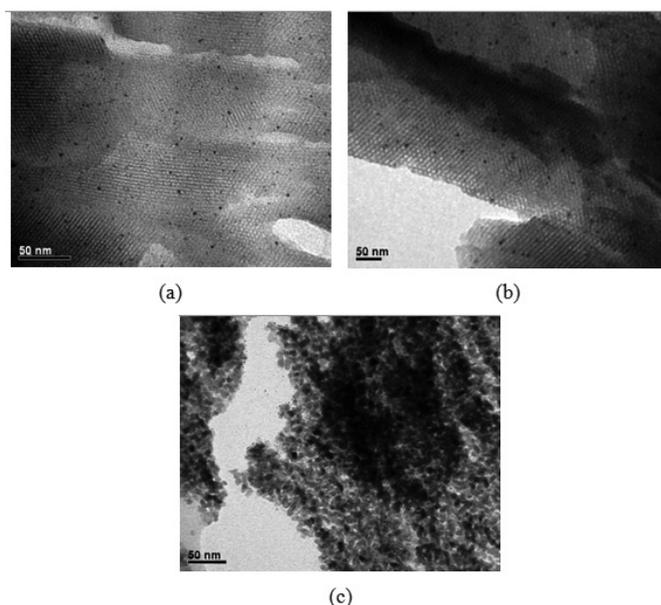


Figure 4. Transmission electron micrographs of Pt/ZrO₂ catalysts a) Pt/NTZrO₂ b)Pt/CNTZrO₂ c) Pt/ZrO₂-P

Catalytic activity in 1-phenyl-1,2-propanedione hydrogenation

Figure 1 shows a scheme of the enantioselective hydrogenation of 1-phenyl-1,2-propanedione. The reaction was studied at 25 °C and 40 bar of H₂ zirconia supported Pt catalysts. It was found that using these systems is possible to induce a preferential formation of (*R*)-1-phenyl-1-hydroxy-2-propanone.

A comparison of the conversion with time for the studied catalyst under the same experimental conditions, temperature of 25°C, hydrogen pressure of 40 bar, catalyst weight 100 mg and modifier concentration 1.0 mM is given in Figure 5. Even though the trends displayed by the catalyst is the same, significant differences in activity can be detected. Thus, to get the same conversion level, i. e. 50% requires, 15 min for Pt/CNTsZrO₂, 40 min for Pt/MSZrO₂ and 100 min for Pt/ZrO₂-P.

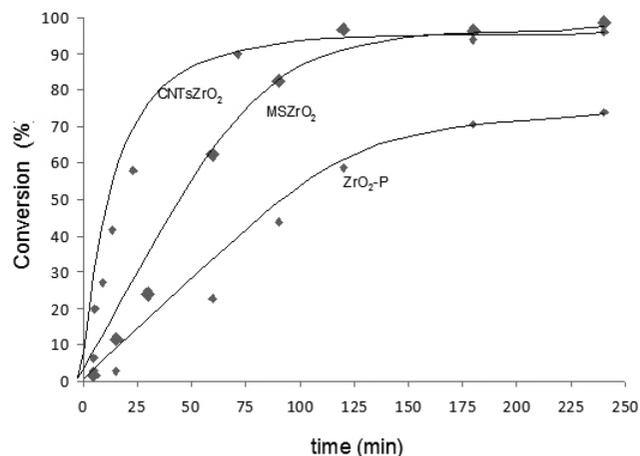


Figure 5. Evolution of the conversion level with time during 1-phenyl-1,2-propanedione hydrogenation on Pt/ZrO₂ catalysts . T= 25°C, P H₂= 40 bar, catalyst weight 100 mg and CD concentration= 0.25 mmol·L⁻¹.

Under the conditions employed the main products were the regioisomers (*R*) and (*S*)-1-hydroxy-1-phenylpropanone. This behaviour may be explained mainly in terms of electronics factors because of the aromatic ring contributes to polarize to a higher extent the C=O bond close to the ring, and therefore the reactions leading to (*R*)-1-phenyl-1-keto-2-propanol and (*S*)-1-phenyl-1-keto-2-propanol; (*E*) (*R*)-1-phenyl-1-keto-2-propanol and (*S*)-1-phenyl-1-keto-2-propanol are less favoured.

Figure 6 shows the evolution of the substrate and products concentration on time during the 1-phenyl-1,2-propanodione hydrogenation on one representative catalyst, at 25 °C, 40 bar of H₂, CD concentration of 2.5 · 10⁻⁴ molxL⁻¹ and 100 mg of 1wt% Pt/CNTsZrO₂ catalyst. The results indicate that under the experimental conditions used here the catalyst is highly active, conversion level close to 80% at 60 min but having a moderate ee and high rs. The evolution of the dione concentration and the various reaction products follow the expected trends, the dione concentration decreases through a first order law, leading to hydroxiketones, (R)- 1-hydroxi-1-phenylpropanone and (S)- 1-hydroxi(R)-1-phenylpropanone as intermediate compounds (B and C in the scheme given in Fig. 1), showing a maximum close to 75 min of reaction for the most active catalyst (Pt/CNTsZrO₂) being larger the time to reach a maximum hydroxiketone concentration for the other catalysts 105 and 150 min for Pt/MSZrO₂ and Pt/ZrO₂, respectively (not shown). The studied catalysts were completely regioselective, because no products generated by the hydrogenation of the C=O bond located far from the aromatic ring were obtained, that means (R)- 2-hydroxi-1-phenylpropanone and (S)- 2-hydroxi-1-phenylpropanone (E and D respectively in the scheme) were not detected. In all cases, the presence of the over hydrogenated products, diols were observed, and the evolution of the concentration of diols, follow the expected sigmoid curve, characteristic of final products of consecutive reactions. Thus, the reaction pathway may be represented by irreversible parallel and consecutive reactions.

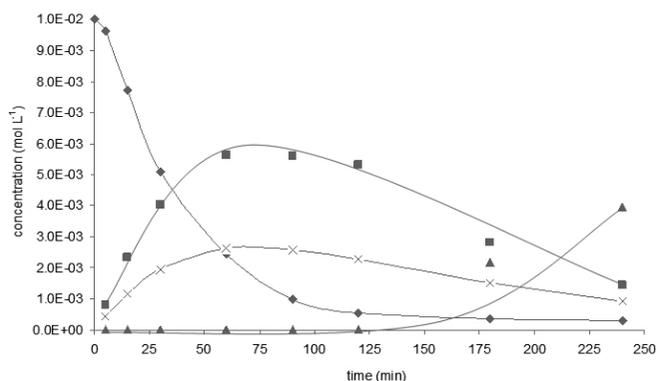


Figure 6. Evolution of the concentration of the substrate and different reaction products during 1-phenyl-1, 2-propanodione hydrogenation. T= 25°C, P H₂= 40 bar, catalyst Pt/CNTsZrO₂ weight 100 mg and CD concentration= 0.25 mmolL⁻¹.

◆ 1-phenyl-1,2-propanedione ■ (R)-1-hydroxi-1-phenyl-2- propanone; X (S)-1-hydroxi-1-phenyl-2- propanone; ▲ Diols

The first order reaction rate constants, denoted as k_g for the consumption of the dione can be easily obtained from $\log C_{A0}C_A$ vs t plots and the respective rate constants k_{IR} and k_{IS} corresponding to the formation of (R)- 1-hydroxi-1-phenylpropanone and (S)- 1-hydroxi(R)-1-phenylpropanone respectively may be obtained from the global first order constant and the ratio of the concentration of these compounds (B and C in the scheme), that is C_B/C_S . Additionally, the reaction rate constants associated to the consecutive reactions, k_{2R} and k_{2S} can be evaluated from the well known equations for intermediates of consecutive reactions, in terms of C_{max} and t_{max} being the former the maximum concentration and the time required to get that level of the corresponding intermediates. The obtained results are summarized in Table 3. It can be seen that the rate constant for the first and second hydrogenation steps (k_1 and k_2) are higher in the Pt catalysts supported in mesostructured supports. This fact may be attributed to the confinement effect produced by the support. The presence of CD in the reaction medium favored the pathway to produce the R-intermediate ($k_{IR} > k_{IS}$) and also in the second step the hydrogenation of the S- intermediate is improved ($k_{2S} > k_{2R}$).

Table 3. First order reaction rate constants, in the hydrogenation of 1-phenyl-1, 2-propanodione at 298 K on Pt/ZrO₂ catalysts.

Catalyst	k_{1g} , 10 ³ min ⁻¹	k_{1R} , 10 ³ min ⁻¹	k_{1S} , 10 ³ min ⁻¹	k_{2R} , 10 ³ min ⁻¹	k_{2S} , 10 ³ min ⁻¹
Pt/MSZrO ₂	1.55	1.01	0.54	8.72	13.2
Pt/CNTsZrO ₂	3.52	2.47	1.05	6.80	17.5
Pt/ ZrO ₂ -P	0.37	0.22	0.15	5.18	9.51

$$k_{1g} = k_{1R} + k_{1S}$$

$$k_{2R} = k'_{2R} + k''_{2R}$$

$$k_{2S} = k'_{2S} + k''_{2S}$$

Considering the previous results obtained in the ethyl pyruvate hydrogenation and also in the 1-phenyl-1, 2-propanodione hydrogenation [7-10,13-18], it would be possible to enhance the yield to the desired products by adjusting CD coverage. For that reason the effect of the CD concentration added at the beginning of the reaction has been studied. Fig. 7 shows the effect of the CD concentration on the evolution of conversion level on time for one of the studied catalysts (1wt% Pt/CNZrO₂ catalyst). Significant differences depending of the CD concentration present in the reaction mixture at the beginning of the reaction can be observed. The curves follow the trends already shown and approach the first order reaction rate. When the reaction is performed in absence of CD, the reaction takes place but at lower reaction rate. Similar behavior was displayed by the other studied catalysts, but obviously having differences in conversion and enantioselectivity levels. Therefore, the CD contributes to the generation of modified catalytic sites which are enantioselective and more active than the metallic sites.

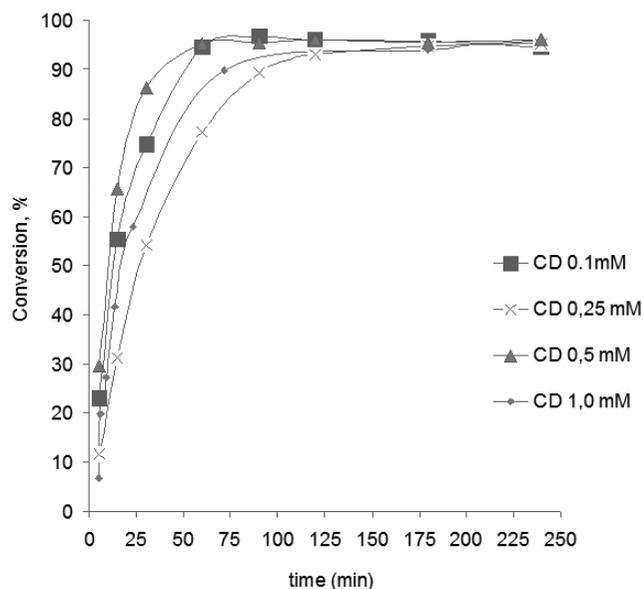


Figure 7. Evolution of conversion level on time in 1-phenyl-1, 2-propanodione hydrogenation. T= 25°C, P H₂= 40 bar, catalyst:1wt% Pt/ CNZrO₂

In Figure 8, the enantiomeric excess to the desired product (R)-1-phenyl-1-hydroxi-2-propanone vs the conversion level obtained on the different catalysts using a same concentration of the chiral modifier (0.50 mmolL⁻¹) is given. It can be seen that the three studied catalysts display similar ee in a wide range of conversion level. These results may be expected taking into account that the reaction is sensitive to metal particle size and the studied catalysts display similar Pt crystal size. The effect of the CD concentration on the enantiomeric excess of the (R)-1-phenyl-1-hydroxi-2-propanone for a representative catalyst is given in Figure 9. The observed trends is similar to those previously reported: a bell-type plot with the maximum corresponding to an ee value of 38% was found showing comparable behavior the three studied catalysts

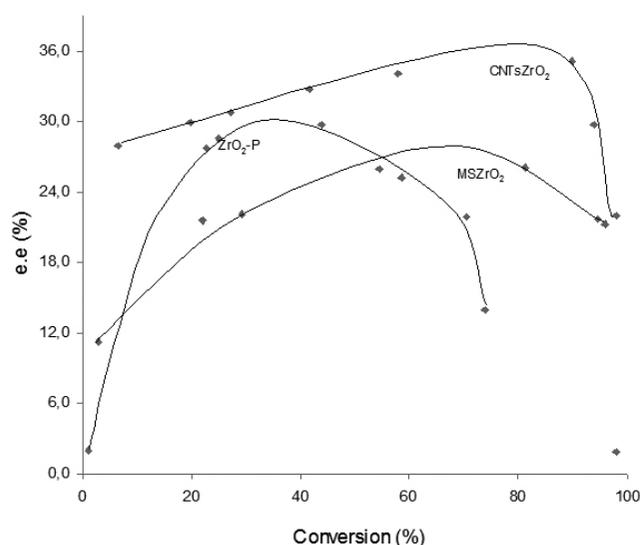


Figure 8. Enantiomeric excess vs conversion level in 1-phenyl-1, 2-propanodione hydrogenation. T= 25°C, P H²= 40 bar, CD concentration = 0.5 mmolL⁻¹ for the studied Pt/ZrO₂ catalysts.

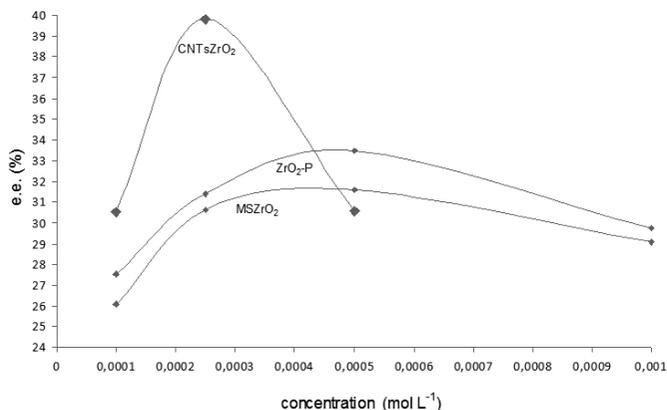


Figure 9. Enantiomeric excess vs cinchonidine concentration in 1-phenyl-1, 2-propanodione hydrogenation. T= 25°C, P H²= 40 bar, for the studied Pt/ZrO₂ catalysts.

The observed behavior confirms that an optimum amount of CD is required to induce chirality. At lower CD concentration the Pt surface coverage is rather limited and consequently leads to lower ee values. As CD concentration increases, also the enantioselectivity increases up to reach an ee maximum. For much higher CD concentration flat adsorption of CD moieties on the metallic surface is highly inhibited, being also possible the formation of CD₂. Both facts made more difficult to induce the desired chirality.

Even though the obtained ee values are rather moderates, confirming the difficulties of this reaction to induce chirality, they are not too far from the best reported values for enantioselectivity in the same reaction [12-19]. The fact that the three studied catalysts display comparable ee values for the hydrogenation of 1-phenyl-1, 2-propanodione, close to 3%, may be understood, taking into account that apart from an optimum inducer concentration, the catalysts require a given metal particle size. It has been published that for similar enantioselective hydrogenation, metallic crystals in the range 2 to 4 nm seems to be the most appropriated [28,32]. The average Pt particle size obtained in the studied zirconium catalysts are in that mentioned range, and therefore no much changes in ee should be expected. However, considering the different pore size of the support, particularly in the mesostructured solids, a confinement effect is expected mainly in that of smaller pore diameter, leading to an important enhancement in the hydrogenation rate, in agreement with the obtained results. In fact, the highest first order reaction constant for the hydrogenation of the

dione is displayed by Pt/CNTZrO₂, followed by Pt/MSZrO₂ and then Pt/ZrO₂ P.

CONCLUSIONS

The obtained results in the hydrogenation of 1-phenyl-1, 2-propanodione on Pt/ZrO₂ catalysts show that not only the nature of the support may affect the catalytic behavior in this reaction but also the porosity of the support. It was demonstrated that mesostructured supports lead to a significant enhancement in the reaction rates due to a confinement effect. The catalysts were completely regioselective. Thus, only the hydrogenation of the C=O bond located near to the aromatic ring took place, and preferentially led to the R-hydroxiketone. The enantiomeric excess of the desired product was similar to the best reported in the literature.

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REFERENCES

1. P. Rylander, Catalytic Hydrogenation over Platinum Metals, Academic Press, New York, 1967.
2. E. Farnetti, M. Pesce, J. Kaspar, R. Spogliarich, M. Graziani, J. Chem. Soc., 1, 746 (1986).
3. G. Allmag, F. Grass, J.M. Grosselin, C. Mercier, J. Mol. Catal., 66, 227 (1991).
4. P. Reyes, H. Rojas, G. Pecchi, J. L. G. Fierro, J. Mol. Catal. A: Chemical 179, 293 (2002).
5. E. Toukoniitty, B. Ševčíková, P. Mäki-Arvela, J. Wärnä, T. Salmi, and D.Yu. Murzin, J. Catal., 213, 7 (2003).
6. P. Reyes, T. Marzioletti, J.L.G. Fierro, Catal. Today, 107-108, 235 (2005).
7. C. H. Campos, J.L.G.Fierro, P. Reyes, J. Chil. Chem. Soc., 52, 1579 (2007).
8. D. Ruiz J.L.G. Fierro, P. Reyes, J. Braz. Chem. Soc. 21(2), 262 (2010).
9. Y. Orito, S. Imai, S. Niwa, G-H.; Nguyen, J. Synth. Org. Chem. Jpn. 37, 173 (1979)
10. Y. Orito, S. Imai, S. Niwa, J. Chem. Soc. Jpn. 1118 (1979).
11. Y. Orito, S. Imai, S. Niwa, J. Chem. Soc. Jpn. 670 (1980).
12. E. Toukoniitty, P. Mäki-Arvela, M. Kuzma, A. Villela, A.K. Neyestanaki, T. Salmi, R. Sjöholm, R. Leino, E. Laine, D.Y. Murzin, J. Catal. 204, 281 (2001).
13. E. Toukoniitty, P. Mäki-Arvela, J. Wärnä, T. Salmi, T.; Catal. Today. 66, 411 (2001).
14. E. Toukoniitty, P. Mäki-Arvela, A. N. Villela, A.K. Neyestanaki, T. Salmi, TR. Leino, R. Sjöholm, E. Laine, E.; J. 14.
15. Väyrynen, P. Kooyman, Catal. Today. 60, 175 (2000).
16. E. Toukoniitty, P. Mäki-Arvela, A.K. Neyestanaki, E. Laine, J.P. Mikkola, T. Salmi, D.Y. Murzin, React. Kinet. Catal. Lett. 3, 73 (2001).
17. E. Toukoniitty, P. Mäki-Arvela, R. Sjöholm, E. Laine, T. Salmi, D. Y. Murzin, React. Kinet. Catal. Lett. 75, 21 (2002).
18. T. Marzioletti, J.L. G. Fierro, P. Reyes P.; Catal. Today, 107, 235 (2005).
19. T. Marzioletti, M. Oportus, D. Ruiz, J.L.G. Fierro, P. Reyes, Catal. Today, 133, 711 (2008).
20. I. Busygin, J. Wärnä, E. Toukoniitty, D.Y. Murzin, R. Leino J. Catal. 254, 339 (2008).
21. D. Gala, D. J. DiBenedetto, J. E. Clark, B. L.; Murphy, D. P.; Schumacher, M. Steinman, Tetrahedron Lett. 35, 611 (1996).
22. P.M. Subramanian, S.K. Chatterjee, M.C. Bhatia, J. Chem. Tech. Biotechnol. 39, 215 (1987).
23. H.U. Blaser, M. Studer, M.; Acc. Chem. Res. 40, 1348 (2007).
24. T. Marzioletti, J.L.G. Fierro, P. Reyes, J. Chil. Chem. Soc. 50 (1), 391 (2005).
25. T.J. Hall, J. El Halder, G.H. Hutchins, R.L. Jenkins, P. McMorn, P.B. Wells and R.P.K. Wells. Topics Catal. 11/12, 167 (2000).
26. U. Böhrer, F. Franke, K. Morgenschweis, T. Bieber and W. Reschitilowski. Catal. Today. 60, 167 (2000).
27. K. Balázsik, B. Török, G. Szakonyi, M. Bartók, Appl. Catal. A: General, 182 (1999).
28. M. A. Fraga, M. J. Mendes, E. Jordão, J. Mol. Catal. A: Chemical. 179, 243 (2002).
29. H.-U. Blaser, H.P. Jalett, D.M. Monti, A. Baiker and J.T. Wehrli, Stud. Surf. Science and Catal. 67, 147 (1991).

30. E. Toukoniitty, B. Sevcikova, N. Kumar, P. Maki-Arvela, T. Salmi, J. Vayrynen, T. Ollonqvist, E. Laine, P. J. Kooyman and D. Y. Murzin., *Stud. Surf. Sci. Catal.* 135, 23 (2000).
31. N. Marín, G. Pecchi, J.L. Margitfalvi, E. Tálas and P. Reyes, *Catalysis in Organic Reactions*, 541 (2005).
32. H. Tsuchiya, P. Schmuki, *Electrochem. Commun.* 6, 1131 (2004).
33. N.M. Marín Astorga, G.Pecchi, J.L.G. Fierro and P. Reyes, *React. Kinet. Catal. Lett.* 87(1), 121 (2006).
34. J.A Czerwinski, F. Szpunar, *Thin Solid Films*, 289, 213 (1996).
35. U. F.M.Ciesla, G. Stucky, F. Schuth, *Chem. Mater.*, 11 ,227 (1999).
36. M. Nakamura, Y. Matsui, *J. Am. Chem. Soc.*, 117, 2651 (1995).
37. P. Reyes, J. Fernández, I. Concha, G. Pecchi, M. López Granados and J.L.G. Fierro, *Catal. Letters* 34, 331, (1995).
38. G. Sierra, J. Barrault, C. Batiot-Dupeyrat, F. Mondragón, *Catal Today*, in press (2009).
39. G. Larsen, E. Lotero, M. Nabity, L. M. Petrovic, D. S. Shobe, *J. Catal.*, 164, 246 (1996).
40. J. L. Blin, R. Flamant, B. L. Su, *Int. J. Inorg. Mat.*, 3, 959 (2001).
41. S.J. Gregg, K. S. W. Sing, in "Physical and Chemical aspects of adsorbents and catalysis", New York: Academic Press, 1970. p. 315.
42. J. S. Beck, J. Vartuli, W. Roth, M. Leonowicz, C. Kresge, K. Schmitt, C. Chu, D. Olson, E. Sheppard, S. McCullen, J. Higgins and J. Schlenker, *J. Am. Chem. Soc.*, 114, 10834 (1992).