

Hydrogenation of carbonyl compounds using tin-modified platinum-based catalysts prepared via surface organometallic chemistry on metals (SOMC/M)

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Abstract

The catalytic behaviour of some compounds containing C=O and/or C=C bonds has been studied over silica-supported platinum-based catalysts, modified with tin. Tin was introduced by means of surface organometallic chemistry on metals (SOMC/M) techniques. The effect of the obtention conditions upon the catalytic performance was evidenced through the study of three systems having the same Sn/Pt atomic ratio (0.4), but prepared and activated at different temperature.

In the hydrogenation of butyraldehyde and butanone, the adsorption of the η^1 -(O) type appears as highly favourable, both from a geometric and electronic point of view. In the benzaldehyde hydrogenation, the increase in the catalytic activity for PtSn-OM and PtSn-BM systems is quite more important than in the PtSn-OM* system, fundamentally by electronic effects associated with the presence of ionic tin and of the phenyl group. In the case of the cyclohexene, geometric and electronic, as well as steric effects lead to a strong reduction of the hydrogenation rate of C=C bond.

These results can be extrapolated to explain the behaviour of the unsaturated α,β -aldehydes. The hydrogenation of the C=O group is promoted and the adsorption modes favourable to the C=C hydrogenation are inhibited by tin. The combination of both effects leads to the sequence of selectivity to UOL: Pt \ll PtSn-OM* < PtSn-BM < PtSn-OM. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In 1912, Paul Sabatier received the Nobel prize of chemistry for his investigations about the use of finely divided metals in hydrogenation reactions. From then on, heterogeneous catalysis in organic chemistry has

been extensively developed. It is well known that the most important role of the metallic catalyst is to generate adsorbed atomic hydrogen, that can be added to several unsaturated bonds: C=C, C=O, C \equiv N, etc. An alternative to this “heterogeneous hydrogen” is the use of inorganic hydrides (LiAlH₄, NaBH₄, etc.) or the generation of hydrogen in “*statu nascendi*” (HCl/Zn).

The hydrogenation of α,β -unsaturated compounds is a reaction with important applications in industrial processes, but quite complex to be fulfilled. This is

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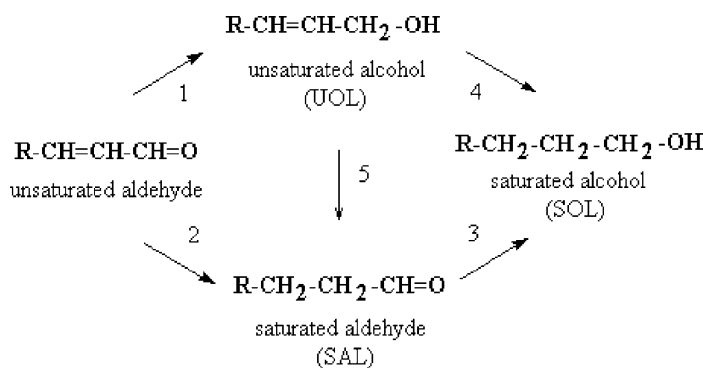


Fig. 1. Reaction pathways for the hydrogenation of α,β -unsaturated aldehydes.

a consequence of the different pathways that the reaction schematised in Fig. 1 for a R-HC=CH-CHO aldehyde can follow [1]. These pathways are: the double C=O bond can react giving an unsaturated alcohol UOL (1), the double C=C bond can be hydrogenated giving a saturated aldehyde SAL (2), and also the $\text{UOL} \rightleftharpoons \text{SAL}$ isomerisation can be produced (5). Finally, the subsequent SAL or UOL hydrogenation leads to the saturated alcohol SOL (3 and 4). The most important product from the industrial point of view is, in most of the cases, the unsaturated alcohol (UOL). This product is also the most difficult to be obtained using transition metals as catalysts, since it is well known that, in general, with these metals the hydrogenation of C=C bond is comparatively easier than that of the C=O bond. For this reason, several efforts have been done to develop strategies that improve the selectivity to UOL, especially by the design of efficient supports [2–5], modification of the metallic particle size [3,6–8] and the addition of selectivity promoters [6,9–13].

Among the transition metals, platinum is one of the most studied and among the selectivity promoters, tin is widely employed due to the good results obtained. The nature of the Pt-Sn bimetallic phase formed, and its influence on the final properties of the catalyst have not been yet well determined and for this, it is still a subject to be debated. The methodology of the addition of tin seems to play an important role on the behaviour of the active phase obtained. Since some years ago, there have been reported methodologies of tin addition by a controlled reaction of organometallic compounds with metal surfaces or metallic oxides, called surface organometallic chemistry on metals

(SOMC/M) [14–19]. These techniques allow the modification of metallic catalysts to obtain bimetallic systems in a controlled manner with specific properties in the hydrogenation of compounds [20–23]. In previous researches performed by our group, SOMC/M has been used to prepare PtSn/SiO_2 catalysts, which presented good results in the selective hydrogenation of crotonaldehyde and cinnamaldehyde [24,25]. The higher selectivity to crotyl alcohol obtained with these catalysts in comparison with the results of catalysts prepared by the classical impregnation methods, evidences how it is possible to improve the efficiency of the catalytic system from the control in the preparation of these catalysts.

When working with molecules containing two double bonds, it is always important to identify which parameters orientates the hydrogenation towards one or the other of these bonds. In the case of the catalytic hydrogenation, it is supposed that the reactive bond is the one involved in the chemisorption on the catalyst surface. The bond of the C=C and C=O groups with the active phase, on the catalyst surface, is the principal factor that determines the selectivity in the hydrogenation of unsaturated α,β -aldehydes. Extensive studies about the adsorption modes of these groups appear in the literature both from the experimental point of view (obtained by the application of different vibrational spectroscopies: FTIR, HREELS and SFGS) as well as by theoretical studies [26–28]. Fig. 2 shows a series of possible adsorbed species determined by spectroscopic studies which are considered well proven [28]. The problem of the chemisorption of aldehydes, ketones and α,β -unsaturated aldehydes has been

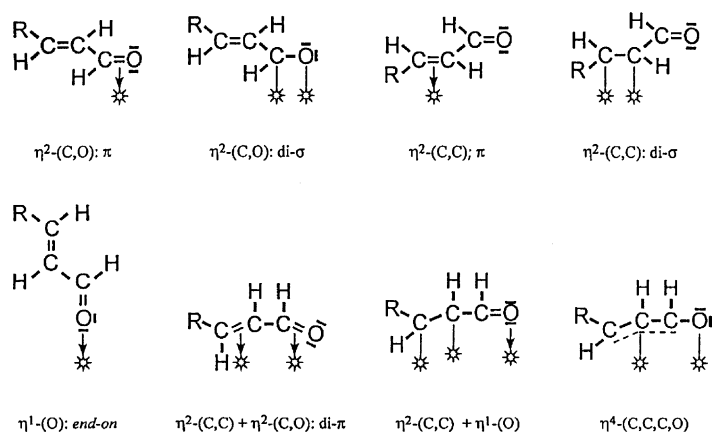


Fig. 2. Possible structures for the adsorption of α,β -unsaturated aldehydes (taken from [23]).

also studied from the point of view of the theoretical chemistry [29,30]. The theoretical analysis there presented showed, among other aspects, that the adsorption modes η^2 -(C,O):di- σ and η^1 -(O):end-on have an existence probability higher than a complex form η^2 -(C,O): π . While the geometry of adsorbed intermediates and the existence of different bonds with the metal surface seem to be well established, the same does not occur with the metallic sites involved in the formation of the different bonds proposed.

Delbecq and Sautet have modelled the adsorption of several unsaturated α,β -aldehydes (acrolein, crotonaldehyde, prenal and cinnamaldehyde) using the extended Hückel approach on platinum and palladium crystals [29]. These authors found that the adsorption mode of the molecule is strongly dependent on the nature of the metal and on the type of exposed face. In this way, on the Pt(111) face a di- σ form is preferably adsorbed, a planar form η^4 on Pd(111) and Pt(100), and on Pt(110) and on Pt(111) steps, a form of the type η^2 -(C,C): π . The selectivity to the unsaturated alcohol is discussed by the authors in terms of the competitive adsorption of the C=C and C=O bonds on the metal surface. This selectivity can be improved by decreasing the binding energy of the C=C bond as a result of an increase of the repulsive electronic interaction with the metal, which may occur due to the presence of substituents on the C=C bond or by the use of metals as Os or Ir, that present more expanded d orbitals. These results indicate that the Pt(111) face that leads to species di- σ type would

be favourable for the obtention of unsaturated alcohol because this adsorption mode favours a selective attack of the C=O bond by the dissociated hydrogen. This suggests that supported platinum catalysts of low dispersion, large particles with high contribution of Pt(111) faces, would lead to higher selectivity values than similar systems, but with high dispersion. For the case of high dispersions (small particles), the percentage of (110) and (100) steps and faces is higher and for this reason adsorption of the planar η^4 -(C,C,C,O) and η^2 -(C,C): π types would be favoured leading to the hydrogenation of both groups in the same way or to the one of the C=C group, respectively.

As it is shown by the antecedents of this theme, both experimental and theoretical, the selectivity to UOL in the catalytic hydrogenation of unsaturated α,β -aldehydes is related to the different possible adsorption modes of the different substrates. The adsorption modes able to promote UOL formation are based on the inhibition of the hydrogenation of the C=C bond or on the promotion of the hydrogenation of the C=O bond. Consequently, it is important to identify which active phases and parameters orientate the hydrogenation towards one or other of the double bonds of the molecule. The knowledge of the specific rates of hydrogenation of C=C and C=O bonds is of great interest to interpret any selectivity change that may occur as a function of the different catalytic systems used. According to this, the aim of this work is to analyse the catalytic behaviour of platinum-based systems in the hydrogenation of some monofunctional

compounds containing C=O and C=C bonds in order to reach a better comprehension of the selective hydrogenation of unsaturated α,β -aldehydes, such as crotonaldehyde and cinnamaldehyde. Catalysts selected for this work were prepared by means of the SOMC/M methodology, which assures the obtention of catalytic phases having a specific interaction between platinum and the organotin compound used as promoter. Special emphasis will be put in determining the effect of the preparation and activation conditions on the resulting catalytic systems. For this reason, three systems were prepared with identical Sn/Pt atomic ratio (Sn/Pt = 0.4), but with different preparation and activation temperatures [24,31].

In order to perform this study, the substrates to be hydrogenated were divided into the following groups: (i) α,β -unsaturated aldehydes; (ii) compounds in which there exists only an aldehydic or ketonic carbonyl group (butyraldehyde and butanone); (iii) compounds where the aldehydic carbonyl group is linked to an aromatic ring (benzaldehyde); (iv) compounds containing double C=C bond (cyclohexene).

2. Experimental

2.1. Catalyst preparation

A Degussa silica (Aerosil 200, $200\text{ m}^2\text{ g}^{-1}$) was used as support. The silica was suspended in $\text{NH}_4\text{OH}_{(\text{aq})}$ under stirring prior to the addition of a $[\text{Pt}(\text{NH}_3)_4]^{2+}$ solution having a concentration so as to obtain 1% w/w Pt exchanged on the silica. The solid was kept under stirring for 24 h at 298 K and then the suspension was separated by filtration under vacuum. The solid was repeatedly washed, dried at 378 K, calcined in air at 773 K and reduced in flowing H_2 at the same temperature, leading to the monometallic Pt/SiO₂ catalyst.

Tin promoted platinum catalysts were prepared with an atomic ratio of Sn/Pt of 0.4. Tin was introduced by means of SOMC/M techniques. To obtain PtSn-OM catalysts, a portion of reduced Pt/SiO₂ was reacted with tetra-*n*-butyltin in *n*-heptane solution under H_2 atmosphere at 363 K. After 4 h of 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, identified as PtSn-OM still had butyl groups grafted to the surface. The bimetallic catalyst PtSn-BM was obtained following the same procedure, eliminating the organic moieties by activation of PtSn-OM catalyst in flowing H_2 at 773 K for 2 h. The sample designated PtSn-OM* was prepared following the same procedure as for PtSn-OM, but the reaction temperature was 423 K and *n*-decane was used as solvent. Once the preparation reaction had finished, a solid without any organic moieties grafted to the surface (without submitting it to any activation step) was obtained. The variation of SnBu₄ concentration and the quantity of hydrocarbons evolved during the preparation reaction were analysed using a Varian 3400 CX gas chromatograph equipped with a flame ionisation detector, employing an 10% OV-101 column (1/8 in. i.d., 0.5 m length). Before being employed, Pt/SiO₂ and PtSn-BM catalysts were treated under flowing H_2 , increasing the temperature from ambient to 773 K, and holding it for 2 h. PtSn-OM and PtSn-OM* catalysts were tested without any further treatment after preparation, and handled without being exposed to the air. Table 1 summarises the conditions of the preparation of the catalysts.

2.2. Catalysts characterisation

The contents of platinum and tin were determined by atomic absorption. H_2 and CO chemisorption was measured in a static volumetric apparatus at ambient

Table 1
Conditions of the preparation of the catalysts

Catalysts	Sn/Pt	SnBu ₄ added (mmol l^{-1})	SnBu ₄ fixed (mmol l^{-1})	BuH/Sn
Pt/SiO ₂	–	–	–	–
PtSn-OM	0.4	1.83	1.05	2.2
PtSn-OM*	0.4	1.04	1.04	3.9
PtSn-BM	0.4	1.83	1.05	4.0

temperature for Pt/SiO₂ and PtSn-BM samples. For each of them, a first hydrogen adsorption isotherm was obtained for the sample previously reduced at 773 K for 4 h and then evacuated at the same temperature overnight. After the first isotherm, the sample was evacuated at ambient temperature and a second isotherm was carried out in the same manner. The difference between the two isotherms extrapolated to zero pressure gave the quantity of the irreversibly adsorbed H₂ and CO. H/Pt and CO/Pt values were calculated assuming an adsorption stoichiometry of unity.

The size distribution of metallic particles was determined by transmission electron microscopy (TEM) using a Jeol 2010 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.

XPS analysis were obtained with an ESCA 750 Shimadzu spectrometer equipped with a hemispherical electron analyser and a Mg K α (1252 eV) X-ray source. Fresh samples were mounted onto a manipulator which allowed the transfer from the preparation chamber into the analysis chamber. PtSn-OM and PtSn-OM* samples were dried and Pt/SiO₂ and PtSn-BM samples were reduced in situ at 673 K for 1 h. The binding energy (BE) of the C 1s peak at 284.6 eV was taken as an internal standard. The intensities were estimated by calculating the integral of each peak after subtraction of the S-shaped background and fitting the experimental peak to a Lorentzian/Gaussian mix of variable proportion.

3. Catalytic tests

The experimental conditions for the catalytic tests were chosen so that the reaction rate was not influenced by mass transfer. Kinetic parameters were routinely measured at short reaction time and conversion values under 10%.

3.1. Hydrogenation of crotonaldehyde and cinnamaldehyde

The hydrogenation of cinnamaldehyde (Aldrich, >99%) and crotonaldehyde (Carlo Erba >99%) were carried out in a batch reactor, magnetically stirred

at 800 rpm, introducing the reactants in toluene and isopropylalcohol solution (0.17 M), respectively. The temperature was kept at 313 K and the pressure at 1 MPa of H₂ during the experiment. The mass of catalyst was 1 and 0.5 g for crotonaldehyde and cinnamaldehyde, respectively. Samples of the reaction products were analysed using a Varian 3400 CX gas chromatograph equipped with a capillary column (30 m \times 0.53 in. i.d., DB Wax bonded phase) and a FID detector.

In order to verify if the catalysts under study were reusable, a series of experiments were carried out with crotonaldehyde as substrate. The procedure consisted of submitting the catalyst to an hydrogenation test, under the experimental conditions previously mentioned. After finishing the reaction, the remaining liquid was separated, the catalyst was repeatedly washed with isopropylalcohol, and it was reused in the hydrogenation of crotonaldehyde.

3.2. Hydrogenation of butyraldehyde, 2-butanone, benzaldehyde and cyclohexene

Butyraldehyde (Aldrich, re-distilled, >99.5%), 2-butanone (Aldrich, >99% spectrophotometric grade), benzaldehyde (Aldrich, re-distilled, >99.5%) and cyclohexene (Aldrich, >99%) were used as received. Hydrogenation experiments were performed in a batch reactor, magnetically stirred at 800 rpm, at a H₂ pressure of 1 MPa, 313 K and 1 g of catalyst (except for benzaldehyde, 0.5 g). The reactants were introduced dissolved in isopropylalcohol, except for benzaldehyde, for which toluene was used (0.17 M). Samples of the reaction products were analysed by gas chromatography, using a Varian 3400 CX gas chromatograph with a 30 m J&W DB-Wax capillary column and a FID detector.

4. Results

Catalysts modified by tin used in this work have been prepared by means of the utilisation of SOMC/M techniques. Table 2 summarises the most important results about the composition and characterisation by XPS and chemisorption of hydrogen and carbon monoxide of the Pt/SiO₂, PtSn-BM, PtSn-OM and PtSn-OM* systems here analysed.

Table 2

Characterisation by XPS and chemisorption of H₂ and CO of Pt/SiO₂, PtSn-BM, PtSn-OM and PtSn-OM* systems

Global stoichiometry of the active phase	Pt/SiO ₂ (Pt)	PtSn-OM (Pt[SnBu _{1.8}] _{0.4})	PtSn-OM* (PtSn _{0.4})	PtSn-BM (PtSn _{0.4})
Sn/Pt	–	0.4	0.4	0.4
H/Pt	0.64	nd	nd	0.21
CO/Pt	0.56	nd	nd	0.25
Binding energy (BE)				
Pt 4f _{7/2}	71.6	70.8	70.6	70.9
Sn(0) 3d _{5/2}	–	487.3	484.6	485.0
Sn(II,IV) 3d _{5/2}	–	487.0	–	487.0
Sn(0)/[Sn(0) + Sn(II,IV)]	–	0.45	1.00	0.67

Systems called PtSn-OM and PtSn-OM* correspond to catalysts prepared by reaction between SnBu₄ and the monometallic catalyst Pt/SiO₂ reduced at 363 and 423 K, respectively. Blank experiments performed at 298 K on silica did not evidence variation in the concentration of SnBu₄ in the impregnating solution. At 423 K, we only observe a slight variation of this concentration with time, with removal of approximately one butane per tin fixed (after 5 h of impregnation it was found less than 250 ppm Sn in the solid). Taking into account that reaction between SnBu₄ and Pt/SiO₂ (Sn/Pt = 0.4) at 423 K is completed before 2 h, with elimination of *ca.* four butane per tin fixed, we can assume that negligible quantities of tin are deposited on silica in PtSn-OM* catalyst.

The PtSn-OM catalyst is a phase whose stoichiometry was determined as Pt[SnBu_{1.8}]_{0.4}/SiO₂, and tin was found as Sn(0) and Sn(II,IV) in similar proportions according to XPS measurements. The PtSn-OM* system consists of the phase having a stoichiometry PtSn_{0.4}/SiO₂, in which tin is found wholly as Sn(0) (Table 2). The system called PtSn-BM is obtained by activation of the PtSn-OM catalyst in H₂ atmosphere at 773 K; in this case, a part of the tin is found as Sn(0) (approximately 70%) and the remaining part is found as ionic tin (Sn(II,IV)). The different organic fragments formed during the activation stage of the catalyst, separated and identified by GC–MS, show that the larger part of the butyl groups (>98%) is removed as butane between 393 and 573 K, with a maximum at 473 K. At temperatures below 393 K, no butane signal was detected [31].

Results of H₂ and CO chemisorption on Pt/SiO₂ showed high H(CO)/Pt values (approximately 0.6) which indicate a high dispersion of the metallic phase.

The bimetallic phase chemisorbs gas up to a ratio of approximately 0.2 H(CO)/Pt. Taking into account that tin is a metal not able to chemisorb H₂ or CO, the values of chemisorbed gas by this phase demonstrate that an appreciable amount of superficial platinum is still present, resulting enough for the catalytic activation in the hydrogenation reactions in which the catalyst is utilised.

4.1. Hydrogenation of crotonaldehyde

Fig. 3a shows the variation of the crotonaldehyde conversion as a function of time for two successive reaction cycles. The curves correspond to Pt/SiO₂, PtSn-BM, PtSn-OM and PtSn-OM* catalysts. A characteristic of these catalytic systems is the stability, only a slight flattening is observed for Pt/SiO₂ catalyst. The presence of tin seems to improve this stability. A behaviour completely reproducible is observed for both cycles, which is an important result principally for the PtSn-OM system, that contains butyl groups anchored to the surface.

The hydrogenation products for crotonaldehyde were: butyraldehyde (SAL), crotyl alcohol (UOL), butanol (SOL), and only at level of traces, cracking products. Selectivities to UOL, SAL and SOL were maintained between cycle and cycle, as it depicted in Fig. 3b for UOL.

With respect to the reaction rate, catalysts modified with tin evidence a marked increase, if compared to the monometallic catalyst. The reaction rate follows the sequence PtSn-OM* > PtSn-BM > PtSn-OM ≫ Pt. Table 3 shows values of overall reaction rate, formation rates of SAL and UOL (estimated between 0 and 10% conversion) and the selectivities to SAL, UOL

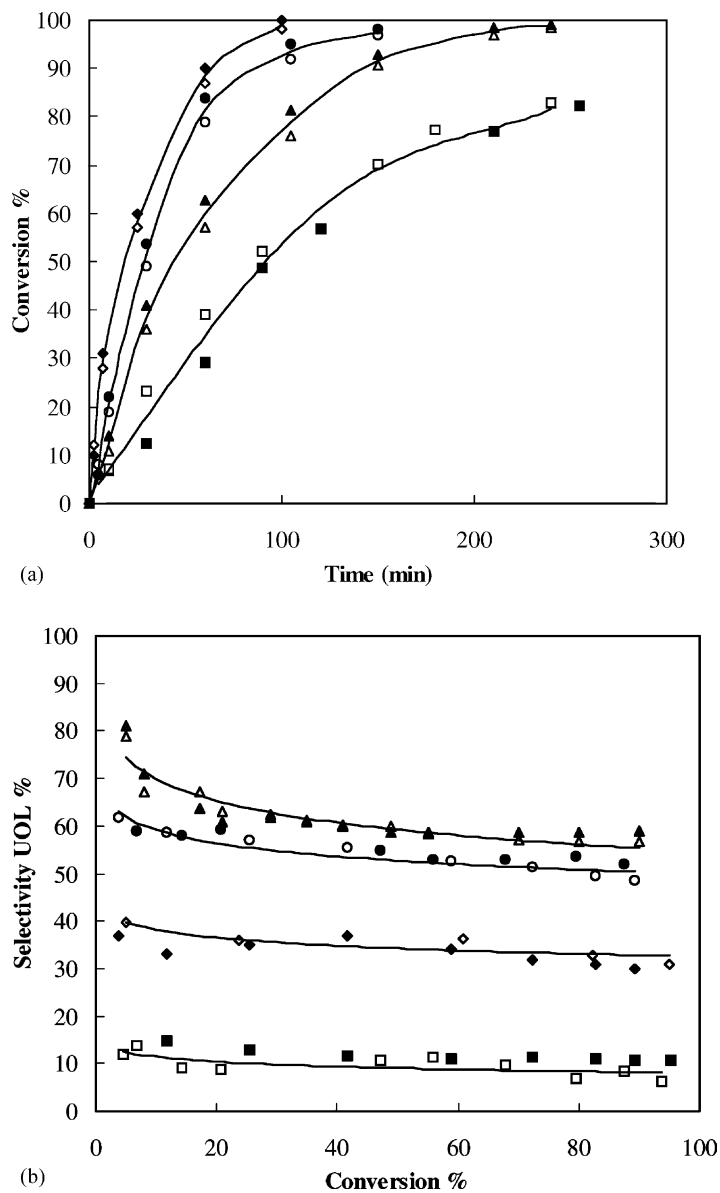


Fig. 3. (a) Variation of crotonaldehyde conversion as a function of time for two successive reaction cycles for Pt/SiO₂ (□: first reaction, ■: second reaction), PtSn-BM (○: first reaction, ●: second reaction), PtSn-OM (△: first reaction, ▲: second reaction) and PtSn-OM* catalysts (◇: first reaction, ◆: second reaction). (b) Hydrogenation of crotonaldehyde. Selectivity of UOL as a function of conversion for Pt/SiO₂ (□: first reaction, ■: second reaction), PtSn-OM (△: first reaction, ▲: second reaction), PtSn-BM (○: first reaction, ●: second reaction) and PtSn-OM* (◇: first reaction, ◆: second reaction).

Table 3
Hydrogenation of crotonaldehyde^a

Catalyst	r_O	r_{UOL}	r_{SAL}	5% conversion			80% conversion		
				SAL	UOL	SOL	SAL	UOL	SOL
Pt	95	65	11	68	11	21	70	7	23
PtSn-OM	390	261	98	25	67	8	21	56	23
PtSn-BM	800	475	288	36	59	5	30	50	20
PtSn-OM*	1370	563	563	42	40	18	38	36	26

^a Formation rate ($\mu\text{mol s}^{-1} \text{g}_{\text{Pt}}^{-1}$) of SAL and UOL (estimated between conversion 0 and 10%), overall reaction rate (r_O) ($\mu\text{mol s}^{-1} \text{g}_{\text{Pt}}^{-1}$) and selectivities to SAL, UOL and SOL at conversion of 5 and 80%.

and SOL at conversions of 5 and 80%. The effect produced by the addition of tin is clearly expressed with these data: the Pt/SiO₂ system gives a S_{UOL} value near 10% for all conversion values; catalysts modified by tin give S_{UOL} values of 67, 59 and 40 at 5% conversion for PtSn-OM, PtSn-BM and PtSn-OM*, respectively.

It is very interesting to analyse results of Table 3 referring to the formation rates of the hydrogenation products of the C=O (UOL) and C=C (SAL) bonds. The presence of tin increases notably, and similarly for the three modified catalysts, the UOL formation rate with respect to the Pt/SiO₂ catalyst. The SAL formation rate is slightly modified in the PtSn-OM catalyst, it increases less markedly than in the case of UOL for PtSn-BM and in similar way to UOL for PtSn-OM*. This effect of tin on the hydrogenation rate of both groups explains the sequence of S_{UOL} , PtSn-OM > PtSn-BM > PtSn-OM*.

4.2. Hydrogenation of cinnamaldehyde

In the molecule of cinnamaldehyde, besides of the double C=C bond and of the C=O group, the benzenic ring is susceptible to be hydrogenated;

hydrogenolysis reactions can also occur. In the presence of isopropylalcohol as solvent, the formation of acetals is observed; for this reason, the catalytic tests were conducted with toluene as solvent. Under the operative conditions used in this work, products that can be assigned to these reactions are not observed. The only products detected at quantifiable levels are cinnamic alcohol (UOL), phenylpropanal (SAL) and phenylpropanol (SOL).

Fig. 4a shows the conversion curves as a function of time for the Pt/SiO₂, PtSn-BM, PtSn-OM and PtSn-OM* systems. As in the case of crotonaldehyde, the shape of these curves is compatible with a good level of stability of the active phases. Only a slight “flattening” is presented by the conversion curve versus time for Pt/SiO₂.

Table 4 shows the catalytic results in the cinnamaldehyde hydrogenation for these systems. Similar to what happens with the crotonaldehyde hydrogenation, in the case of the monometallic catalyst, the major product is the saturated aldehyde, and the S_{UOL} is maintained under 20%. The addition of tin produces a noticeable change in the distribution of products and in the reaction rate: the S_{UOL} is high

Table 4
Hydrogenation of cinnamaldehyde^a

Catalyst	r_O	r_{UOL}	r_{SAL}	5% conversion			80% conversion		
				SAL	UOL	SOL	SAL	UOL	SOL
Pt	662	113	450	68	17	15	65	12	23
PtSn-OM	2197	1750	425	19	80	1	15	60	25
PtSn-BM	1510	1188	325	23	74	3	14	58	28
PtSn-OM*	1360	638	638	40	54	6	44	37	19

^a Formation rate ($\mu\text{mol s}^{-1} \text{g}_{\text{Pt}}^{-1}$) of SAL and UOL (estimated between conversion 0 and 10%), overall reaction rate (r_O) ($\mu\text{mol s}^{-1} \text{g}_{\text{Pt}}^{-1}$) and the selectivities to SAL, UOL and SOL at conversion of 5 and 80%.

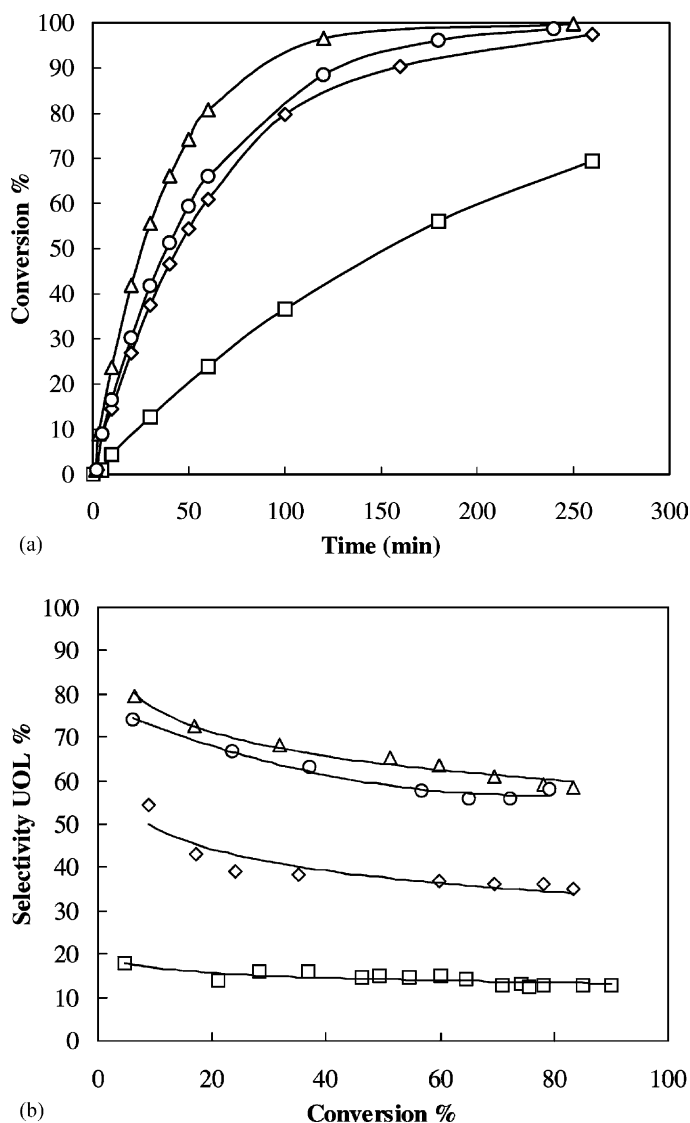


Fig. 4. (a) Conversion of cinnamaldehyde as a function of time for Pt/SiO₂ (□), PtSn-OM (△), PtSn-OM* (◇) and PtSn-BM (○) catalysts. (b) Hydrogenation of cinnamaldehyde. Selectivity of UOL as a function of conversion for Pt/SiO₂ (□), PtSn-OM (△), PtSn-BM (○) and PtSn-OM* (◇).

in the complete interval of conversions, while the S_{SAL} varies slightly with the conversion and the S_{SOL} increases with the conversion due to the consecutive reactions of total hydrogenation of SAL and UOL. Fig. 4b shows the variation of S_{UOL} as a function of conversion for the four catalysts studied.

When the modifying effect of tin is analysed in the different catalytic systems, based on the forma-

tion rates of products, some differences appear with respect to the crotonaldehyde hydrogenation. In the cinnamaldehyde, the hydrogenation rate of the carbonyl group (UOL formation) is strongly favoured for PtSn-OM and PtSn-BM; in this case, the sequence is PtSn-OM > PtSn-BM > PtSn-OM*. Instead, in the hydrogenation of the double C=C bond (SAL formation), a slight reduction for PtSn-OM and PtSn-BM is

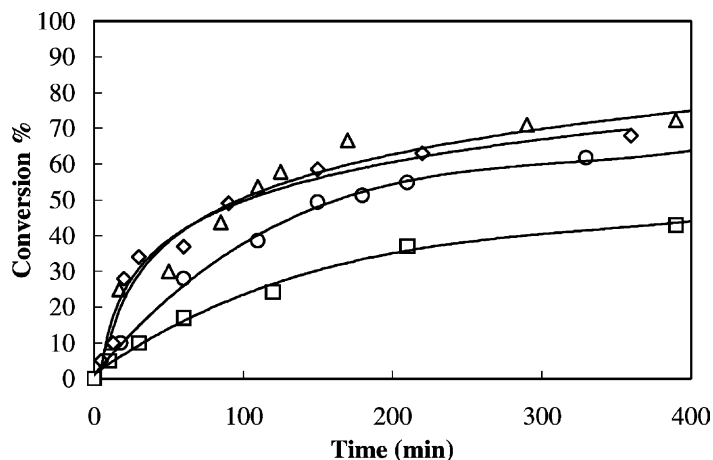


Fig. 5. Conversion of butyraldehyde as a function of time for Pt/SiO₂ (□), PtSn-OM (△), PtSn-OM* (◇) and PtSn-BM (○) catalysts.

observed with respect to Pt/SiO₂, while the PtSn-OM* system presents an increase at this rate. This ratio between the formation rates of products explains the high *S*_{UOL} that is reached for the PtSn-OM catalyst.

4.3. Hydrogenation of butyraldehyde and butanone

The hydrogenation of butyraldehyde and butanone leads to the formation of the corresponding alcohol. Fig. 5 shows the hydrogenation results of butyraldehyde on the catalysts studied. As it can be observed, the addition of tin favours the production of 1-butanol.

Analogous results were obtained with butanone (Fig. 6), noting that in all cases, the reactivity of ketonic carbonyl is higher than the one of the aldehydic carbonyl, which is in agreement with results obtained in the literature for the hydrogenation of other aldehydes and ketones on supported metallic catalysts [32]. A behaviour difference is shown with what happens in the presence of homogeneous catalysts, with which the monofunctional aldehydes result to be more reactive than the monofunctional ketones [33].

Table 5 shows the values of reaction rate measured at conversions between 0 and 10% for the

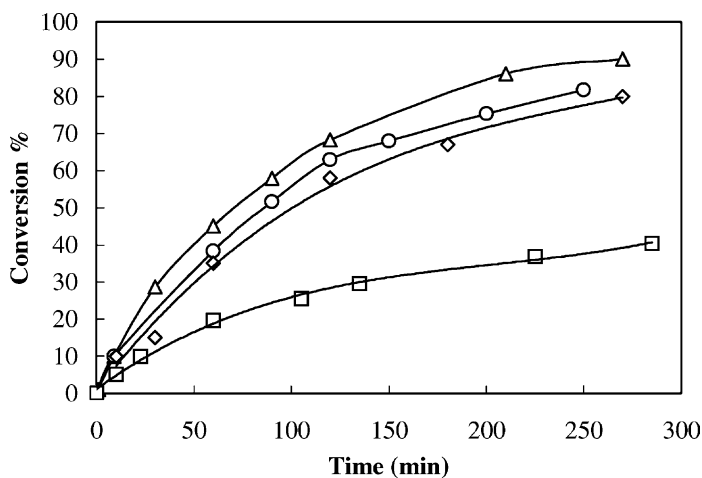


Fig. 6. Conversion of butanone as a function of time for the Pt/SiO₂ (□), PtSn-OM (△), PtSn-OM* (◇) and PtSn-BM (○) catalysts.

Table 5

Reaction rate ($\text{mmol s}^{-1} \text{g}_{\text{Pts}}^{-1}$) for the hydrogenation of butanal, butanone, benzaldehyde and cyclohexene, measured at conversions between 0 and 10%

Catalyst	Butyraldehyde	Butanone	Benzaldehyde	Cyclohexene
Pt/SiO ₂	53	70	64	850
PtSn-OM	138	175	425	25
PtSn-BM	88	175	425	63
PtSn-OM*	125	163	88	638

hydrogenation of butyraldehyde and butanone. It is observed that the catalytic activities of the three tin-modified systems (PtSn-BM, PtSn-OM and PtSn-OM*) are very similar among them and higher than the one of Pt/SiO₂.

When comparing these hydrogenation rates of the carbonyl group in the monofunctional substrates with the ones of the carbonyl group in the crotonaldehyde (UOL production rate), it is observed that in the α,β -unsaturated aldehyde, this rate results appreciably higher.

The plots conversion versus time for butyraldehyde and for butanone (Figs. 5 and 6) present a certain “flattening”, more pronounced for Pt/SiO₂ than for the systems modified by tin. This type of curves would indicate a deactivation process more important in the hydrogenation of monofunctional carbonyl groups than in the α,β -unsaturated aldehydes, since this “flattening” is almost imperceptible in the curves corresponding to the crotonaldehyde hydrogenation (Fig. 3a). On the other hand, the deactivation phenomenon seems higher for butyraldehyde than for

butanone and, in all cases, the addition of tin leads to a lower deactivating effect on the active phase.

4.4. Hydrogenation of benzaldehyde

Fig. 7 shows the results of benzaldehyde hydrogenation on Pt/SiO₂, PtSn-BM, PtSn-OM and PtSn-OM*. In all cases, the only detected product was the benzyl alcohol. The presence of benzene as traces could not be discarded, since in the conditions of chromatographic analysis and in the presence of toluene as solvent, it would not be detectable. For the monometallic system, and to a lower extension for PtSn-OM*, a certain catalyst deactivation is observed, while for PtSn-OM and PtSn-BM, the deactivation level is almost negligible.

The reaction rates follow the sequence PtSn-OM \approx Pt-Sn-BM > PtSn-OM* > Pt/SiO₂ (Table 5). The reaction rate of the benzaldehyde decreases noticeably for the PtSn-OM* system with respect to PtSn-BM and PtSn-OM. These results are analogous with respect to the values of the hydrogenation rate of the C=O group for the cinnamaldehyde, where an important decrease

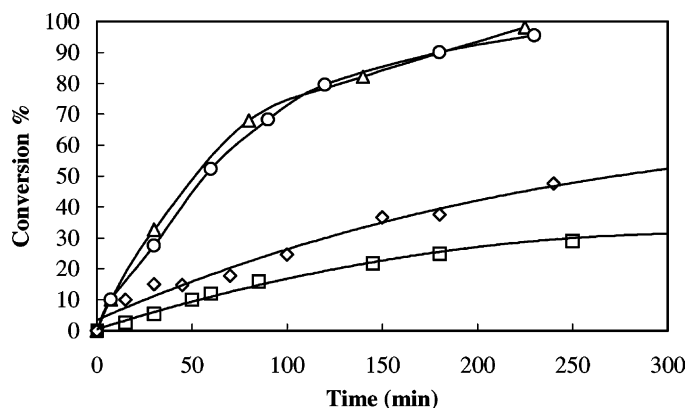


Fig. 7. Conversion of benzaldehyde as a function of time for Pt/SiO₂ (□), PtSn-OM (△), PtSn-OM* (◇) and PtSn-BM (○) catalysts.

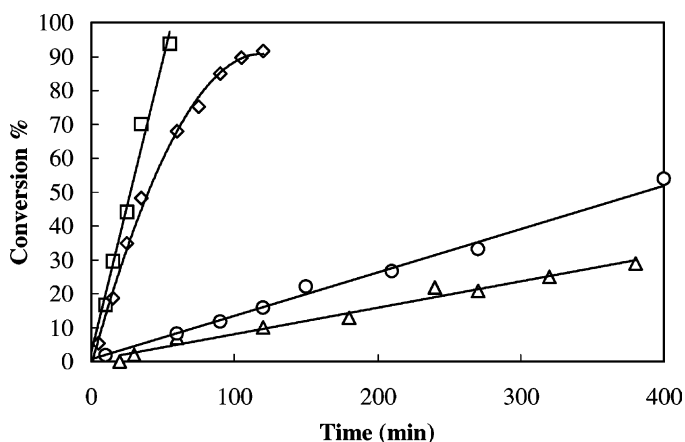


Fig. 8. Conversion of cyclohexene as a function of time for Pt/SiO₂ (□), PtSn-OM (△), PtSn-OM* (◇) and PtSn-BM (○) catalysts.

was also observed in the UOL formation rate for the PtSn-OM* system (see Table 4).

As in the case of crotonaldehyde, when comparing the reaction rates of the benzaldehyde with respect to the ones of the UOL formation in the cinnamaldehyde, a high decrease is observed in the values of the corresponding rates for the monofunctional aldehyde.

4.5. Hydrogenation of cyclohexene

The cyclohexene hydrogenation provides information about the behaviour of the analysed catalysts with respect to the hydrogenation of C=C bonds. For all the systems, the only product observed is the cyclohexane. Kinetic results (conversion versus reaction time) presented in Fig. 8 indicate that, different to what happens in the monofunctional aldehydes and ketones, the deactivation process is not important. As it was expected, reaction rates follow a sequence that is completely different to the one of those compounds; Pt/SiO₂ > PtSn-OM* >> PtSn-BM > PtSn-OM (Table 5). The reaction rate for the monometallic system is one order of magnitude higher than for the PtSn-OM system. Concerning the comparison between the systems modified by tin, there exists a coincidence in the tendencies observed, for the unsaturated aldehydes (SAL formation rate) as well as for the monofunctional olefinic compound. The hydrogenation rates of the C=C group are always higher for the PtSn-OM* system.

The behaviour of the different active phases with respect to the substrates is compatible with the

modifications observed by the addition of tin to platinum in the hydrogenation of α,β -unsaturated aldehydes. The hydrogenation rates of carbonyl bonds increase and the hydrogenation rates of olefinic groups decrease, giving rise to the obtention of higher selectivities to unsaturated alcohols, according to the sequence PtSn-OM > PtSn-BM > PtSn-OM* >> Pt/SiO₂.

5. Discussion

5.1. Characterisation

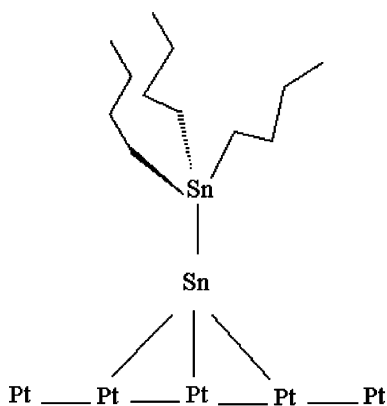
The monometallic catalyst Pt/SiO₂ presents a homogeneous distribution of the particle size between 1 and 3 nm, and a H/Pt ratio near 0.6 indicating a high dispersion value. The addition of tin via SOMC/M produces a slight increase of the particle size, which should not be assigned to the sintering of platinum, but to a selective deposit of tin on it. Particles are small enough so as not to expect a favourable effect on the selectivity to UOL in the hydrogenation of α,β -unsaturated aldehydes, according to [1]. For this reason, the increase observed in the values of such selectivity as well as in the hydrogenation rate of the monofunctional compounds should be assigned exclusively to the modification of the active site by the presence of tin.

The values of H₂ and CO chemisorption decrease from 0.6 to 0.2–0.3 when passing from Pt/SiO₂ to

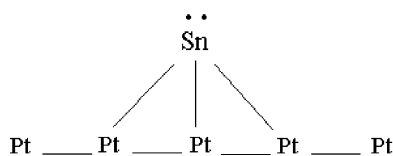
PtSn-BM. It is accepted that this decrease is produced by electronic and geometrical effects introduced by tin when it is deposited on platinum. The geometrical dilution effects are easily comprehensible, while the electronic effects are explained by the variation in the heats of adsorption determined on Pt and PtSn systems. Cortright and Dumesic demonstrated by microcalorimetric studies that the addition of tin to platinum supported on silica or L-zeolite is responsible for an important decrease in the heat of the H₂ and CO adsorption as well as of their chemisorbed amount [34]. Similar results are reported by Claus for Rh and RhSn on silica prepared from SOMC/M techniques [23].

XPS results evidence the different nature of the active phases as a function of the operation conditions in which the preparation is carried out. In all cases, the modified systems show identical tin concentration (Sn/Pt = 0.4). When the preparation temperature is 363 K, some butyl groups remain linked to the tin that has reacted with the superficial platinum. This tin is found in ionic and metallic state in similar proportions (PtSn-OM). The active site architecture, as it was proposed in a previous work [24], is presented in Scheme 1. These type of surface entities have been proposed by Margitfalvi et al. (“multilayered tin organometallic surface species”) [19] and Didillon et al. (“new surface organometallic materials”) [21].

When the preparation temperature is 423 K all butyl groups are removed, tin (found as Sn(0) in this case) would be as adatom “decorating” the platinum surface (PtSn-OM*) and the active site, in this situation,



Scheme 1. Proposed supported phase (PtSn-OM) formed by reaction between Pt/SiO₂ and SnBu₄ at 363 K.



Scheme 2. Proposed supported phase (PtSn-OM*) formed by reaction between Pt/SiO₂ and SnBu₄ at 423 K.

would correspond to that of Scheme 2. A PtSn-OM catalyst, in the presence of hydrogen and at high temperatures (773 K) loses all the alkyl groups still attached to the surface (PtSn-BM), being transformed in a system where, as it was determined by XPS, platinum is found in metallic state and tin in metallic and ionic state in an approximate 70/30 ratio, respectively (Table 2). The ionic tin (Sn(II,IV)) is probably obtained by migration to the metal-support interface in which it would be present as SnO_x, while Sn(0) would form PtSn superficial alloys.

An interesting aspect arises from the BE analysis of platinum shown in Table 2. In the three systems modified by tin, a shift is observed in the BE towards lower values of approximately 1 eV with respect to Pt/SiO₂, this shift can be interpreted as an electronic transfer from tin to platinum. These modifications strengthen the hypothesis of the electronic effects induced by tin as it was previously discussed to explain changes in the H₂ and CO chemisorption. The increase in the electronic density of platinum is observed not only in the systems where tin is in ionic state, but also in the case of the PtSn-OM* catalyst (100% of Sn(0)). For this reason, it is acceptable to propose that even in the case of the metallic tin forming superficial alloys, polarised states of Pt^{δ-} and Sn^{δ+} are generated, which would be important in the chemisorption of reagents containing double C=O and C=C bonds, and in the competence among them [30].

5.2. Stability of the catalysts

From the study of the catalytic properties of these systems, the stability of the active phases is transcendental in successive cycles. This is demonstrated by the repeatability observed for the crotonaldehyde hydrogenation in the conversion values as well as in the ones of the different selectivities (Fig. 3a and b). These stability results are of special interest for the case of the

PtSn-OM (Pt[SnBu_{1.8}]_{0.4}) phase, where, if the detachment of organic fragments were produced during the reaction stage, this would provoke changes in the conversion curves and/or selectivity versus time. These changes do not occur, and taking into account the reaction temperature (313 K) and the previously stated GC–MS results, the stability of this type of supported organobimetallic phases could be accepted, which represents a fundamental aspect for their application in the area of chemo-, regio- and stereo-selectivity, important in fine chemistry. Analogous results concerning the stability of organobimetallic phases have been reported by the group of professor Basset, mainly in the case of RhSn catalysts for hydrogenation reactions [20].

According to works recently published [35–38], a process of deactivation or poisoning in the hydrogenation of unsaturated or monofunctional aldehydes is expected due to the irreversible CO adsorption by decarbonylation or by the formation of oligomers that remain adsorbed on the active phase. Processes of this nature have to be present in this study as it arises from the “flattening” shown by the conversion versus time curves, compatible with a simultaneous deactivation mechanism, and accepting that the global reaction order with respect to the substrate is zero or near zero [39].

The decarbonylation reactions occur very quickly, and even in a small extension, the CO generated can produce the irreversible poisoning of active sites. However, this poisoning would be fast and would not explain the mentioned slight “flattening”, at least for the monometallic catalyst in the case of the crotonaldehyde hydrogenation, taking into account results of Fig. 3a, where it is observed that for Pt/SiO₂, the catalytic performance is repeated between two successive cycles. The catalyst is washed between these two cycles at room temperature, and this could remove the reversible poisoning, e.g. the oligomers formed during the first test, but not the CO that is irreversibly chemisorbed. Therefore, although an initial deactivation can exist by irreversible decarbonylation affecting both cycles, a reversible deactivation by polymerisation via aldolic condensation seems to be the most probable mechanism to explain the type of curves observed.

The deactivation level mentioned is well evidenced for butyraldehyde and butanone, it is less important for

benzaldehyde and it is not observed for cyclohexene. This tends to validate the hypothesis about the formation of oligomers, based on the condensation reactions, whereas in the case of benzaldehyde the non-existence of H in a α position reduces the possibility of these reactions. The knowledge of the mechanisms of poisoning by decarbonylation or polymerisation is very important to prevent the phenomenon as well as to comprehend the general mechanism of hydrogenation of compounds on these systems. With this aim, we have started a systematic study of successive catalytic cycles with different oxidising and reducing treatments at different temperatures, coupled to other characterisation techniques as, e.g. DRIFTS.

It is clear that the presence of tin modifier decreases notably the deactivation level for all the compounds studied, monofunctional and unsaturated. In the case of α,β -unsaturated aldehydes, the effect of tin deposited via SOMC/M in any of the three types of catalysts minimises notably the deactivation during the test as it is suggested by the linearity of the conversion versus time curves.

5.3. Activity and selectivity

When analysing the behaviour in the hydrogenation of butyraldehyde and butanone, different from what happens in homogeneous catalysis, where monofunctional aldehydes result to be more active than monofunctional ketones [33], the reactivity of the ketonic carbonyl is higher than the one of the aldehydic carbonyl for the four catalysts tested (see values of catalytic activity in Table 5). This result is in agreement with data obtained in the literature for the hydrogenation of other aldehydes and ketones on supported metallic catalysts [32]. A reasonable explanation for this effect is that the adsorption mode η^1 -(O) on the metallic phase through the O atom on an active site (“end-on”, Fig. 2) is more reactive than the adsorption mode η^2 -(C,O) on two sites (Fig. 2), having the η^2 -(C,O) mode higher probability in the adsorption of butyraldehyde than in that of butanone.

The addition of tin increases the hydrogenation rate for all the compounds studied. For butanone and butyraldehyde, the increase is similar in any of the systems (PtSn-OM, PtSn-BM or PtSn-OM*). All the catalysts modified with tin present a dilution of platinum sites and an adsorption of the type η^1 -(O) is

more probable on this type of surface, which is more favourable for the adsorption of butanone. Although these effects of geometrical nature play an important role in the catalytic activity observed, electronic modifications must not be discarded. As it was previously mentioned, according to the BE's shift measured by XPS (see Table 2), PtSn-OM and PtSn-BM systems show the presence of the ionic tin and the PtSn-OM* system presents tin with a positive charge density. This type of phases, from the electronic point of view, appear highly favourable for η^1 -(O) and η^2 -(C,O) adsorptions with simultaneous weakening of the C=O group stability and, in this way, higher easiness and hydrogenation rate to alcohol. The existence of an induced selectivity improvement due to the variation in the ionic state of tin during reaction, as it was proposed in literature [40], could not be discarded, although the fact of the repetitive performance of the reused catalysts seems to support the idea that this effect should not be very important in our case.

The hydrogenation rates of the benzaldehyde to benzyl alcohol are strongly improved on the PtSn-OM and PtSn-BM systems. The non-hydrogenation of the aromatic ring can be assigned to the coexistence of mild conditions employed and steric factors that prevent the ring adsorption in a planar form on the catalyst surface. The influence of electronic effects seems to be fundamental although it must be admitted that in the PtSn-OM system the presence of alkyl groups must produce a steric effect very favourable for the adsorption modes involving the C=O group via the O atom. The increase in the catalytic activity showed by the systems presenting ionic tin (PtSn-OM and PtSn-BM) is more important than in the case of the PtSn-OM* system, in which there is not ionic tin, but it would be found as positively polarised.

When comparing system by system, the hydrogenation rate of benzaldehyde is always higher than the one of butanone or the one of the butyraldehyde. This behaviour is in agreement with the inductive effect of the phenyl group that produces a decrease in the bonding energy of the C=O group with respect to the aliphatic compounds as it is proved by IR spectroscopy, where the stretching band of C=O passes from 1720 to 1740 cm^{-1} in the aliphatic aldehydes (R-CH₂-CHO) to 1695–1715 cm^{-1} in the aromatic aldehydes (Ar-CHO).

The geometrical effect of platinum dilution by tin and the increase in the electronic density on the platinum atoms giving rise to a strong Pauli repulsion [30] (for all the catalytic systems), as well as the steric effects (PtSn-OM) allow the comprehension of the behaviour of these systems with respect to the hydrogenation of C=C groups (cyclohexene, Pt > PtSn-OM* \gg PtSn-BM > PtSn-OM). Probably, the result more difficult to be explained is the activity fall observed for PtSn-OM* in relation to PtSn-BM (638 and 63 $\text{mmol s}^{-1} \text{g}_{\text{Pt}}^{-1}$, respectively). However, in this case an analysis can also be made that based on results of theoretical modelling of the adsorption on different platinum surfaces leads to a reasonable interpretation of this phenomenon. This work [30] showed that on the (1 1 0) surface and on the steps or edges on the (1 1 1) surface, Pauli repulsion effects are hence reduced in the η^2 -(C,C): π adsorption mode (mode that contributes strongly to the hydrogenation of C=C) in relation to the dense (1 1 1) surface. Taking into account the Scheme 2 proposed for PtSn-OM*, where all the tin is found as Sn(0) “decorating” the platinum surface, it could be admitted that this increases the participation of platinum sites quite similar to the ones participating on the (1 1 0) surface and on the steps or edges on the (1 1 1) surface.

In the case of unsaturated aldehydes, as it occurs with butyraldehyde, butanone or benzaldehyde, the hydrogenation rate of the C=O group (UOL production) shows a noticeable increase in catalysts modified with tin, with respect to the monometallic catalyst. In the systems modified with tin, the dilution favours the presence of species of the types η^1 -(O) and η^2 -(C,O) in crotonaldehyde and, due to the molecule geometry, it favours the presence, in a more noticeable way, of the form η^1 -(O) type for cinnamaldehyde. These species favour the hydrogenation of the C=O group. This dilution must inhibit other forms of chemisorption competitive with the previous ones, as, e.g. of the types η^2 -(C,C) and (η^2 -(C,O) + η^4 -(C,C,C,O)), favourable for the hydrogenation of the C=C group, this leading to a lower SAL production. These results follow a tendency similar to the ones mentioned for cyclohexene, where the chemisorbed intermediates of the type η^2 -(C,C) would be electronically and geometrically less promoted according to the sequence Pt \ll PtSn-OM* < PtSn-BM < PtSn-OM, in coincidence

with the determined values of the hydrogenation rate.

It is evident that the geometrical modifications introduced by tin in any of the analysed systems (PtSn-BM, PtSn-OM and PtSn-OM*) tend to promote the adsorption of intermediates leading to unsaturated alcohol. However, as it was proposed for the monofunctional substrates, the electronic effects must be also important in the chemisorption of the reaction intermediates. In this case, as in the case of the phenyl group, the presence of the conjugated C=C group tends to facilitate the hydrogenation of the C=O group to >C–OH. The values of the stretching band for C=O are 1680–1690 cm⁻¹ and 1720–1740 cm⁻¹ for R–HC=CH–HC=O and R–H₂C–CH₂–HC=O, respectively. In the case of the cinnamaldehyde, that has a phenyl group and a C=C group conjugated to the C=O group, these electronic effects are more important than in the crotonaldehyde. The existence of sites type “Lewis acid sites” (electronic modifications), due to the presence of Sn^{δ+} and ionic tin, tends to promote the H₂ attack to the C=O group and in this way, it leads to the obtention of higher formation rate and selectivity to the unsaturated alcohol. This type of electronic modifications seems to play a fundamental role for molecules with phenyl groups, as in the case of the cinnamaldehyde. The presence of ionic tin seems to be the responsible for the increase in the UOL formation rate, more important for the PtSn-OM and PtSn-BM systems than for the PtSn-OM*. This is different for the case of the crotonaldehyde where the UOL formation rates are of the same order for PtSn-OM, PtSn-OM* and PtSn-BM (Table 3). In the PtSn-OM and PtSn-BM systems, taking into account XPS studies that reveal the presence of ionic Sn, it is observed that the ratios of ionic tin to total tin are directly related with the hydrogenation rates of the cinnamaldehyde to cinnamyl alcohol. An analogous behaviour was observed for the benzyl alcohol from the benzaldehyde where the production rate of such alcohol on PtSn-OM and PtSn-BM catalysts is higher than on the PtSn-OM* catalyst. Taking into account the speculative hypothesis made for butanone and butyraldehyde, referring to the higher reactivity of species η¹-(O) versus η²-(C,O), these results could be explained by the Snⁿ⁺ preferential promotion, of the most reactive intermediate of the η¹-(O) type, that it

would be the major contribution for the cinnamaldehyde.

6. Conclusions

- The importance of establishing adequate conditions for the preparation of catalysts was pointed out. All samples used were modified with the same SnBu₄ (Sn/Pt = 0.4) concentration, only varying the preparation or activation temperature. According to TEM, CO and H₂ chemisorption, and XPS measurements, the addition of tin produces a dilution of the platinum phase and has a modifying effect on the electronic characteristics: the electronic density of platinum increases and tin appears as Sn(II,IV) and Sn(0) (PtSn-OM and PtSn-BM) as well as Sn(0) (PtSn-OM*).
- In the hydrogenation of butyraldehyde and butanone using catalysts modified by tin, the adsorption of the η¹-(O) type appear as highly favourable due to a geometric effect as well as by an electronic point of view, by the presence of ionic tin and/or positively polarised tin.
- In the benzaldehyde hydrogenation, the increase in the catalytic activity for PtSn-OM and PtSn-BM systems is quite more important than in the PtSn-OM* system, fundamentally by electronic effects associated with the presence of ionic tin and of the phenyl group.
- In the case of the cyclohexene, geometric and electronic effects (important Pauli repulsion) as well as steric effects lead to a strong reduction of the hydrogenation rate according to the order PtSn-OM* ≫ PtSn-BM > PtSn-OM.
- The activity patterns obtained on the different catalytic systems with monofunctional substrates can be extrapolated to explain the behaviour of the α,β-unsaturated aldehydes studied in this work. In the systems modified by tin, especially PtSn-OM and PtSn-BM, the adsorption modes η¹-(O) and η²-(C,O) result to be favoured and they promote the hydrogenation of the C=O group. Parallely, the adsorption modes favourable to the C=C hydrogenation are inhibited with a lower SAL production. The combination of both effects leads to a sequence of selectivity to UOL on the studied catalysts: Pt ≪ PtSn-OM* < PtSn-BM < PtSn-OM.

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References

- [1] P. Gallezot, D. Richard, *Catal. Rev.-Sci. Eng.* 40 (1998) 81.
- [2] M.A. Vannice, B. Sen, *J. Catal.* 115 (1989) 65.
- [3] P. Gallezot, A. Giroir-Fendler, D. Richard, *Catal. Lett.* 5 (1990) 169.
- [4] D.G. Blackmond, R. Oukazi, B. Blanc, P. Gallezot, *J. Catal.* 131 (1991) 401.
- [5] M. Englisch, A. Jentys, J.A. Lercher, *J. Catal.* 166 (1997) 25.
- [6] D. Richard, P. Fouilloux, P. Gallezot, in: *Proceedings of the 9th International Congress on Catalysis*, Vol. 3, Ottawa, Canada, 1988, p. 1074.
- [7] S. Galvagno, G. Capannelli, G. Neri, A. Donato, R. Pietropaolo, *J. Mol. Catal.* 64 (1991) 237.
- [8] S. Galvagno, C. Milone, A. Donato, G. Neri, R. Pietropaolo, *Catal. Lett.* 18 (1993) 349.
- [9] Z. Poltarzewski, S. Galvagno, R. Pietropaolo, P. Staiti, *J. Catal.* 102 (1986) 190.
- [10] D. Goupil, P. Fouilloux, P. Gallezot, *React. Kinet. Catal. Lett.* 35 (1987) 185.
- [11] C.G. Raab, M. Englisch, T.B.L.W. Marinelli, J.A. Lercher, *Stud. Surf. Sci. Catal.* 78 (1993) 211.
- [12] F. Coloma, A. Sepúlveda-Escribano, J.L.G. Fierro, F. Rodríguez-Reinoso, *Appl. Catal. A: Gen.* 136 (1996) 231.
- [13] F.B. Passos, M. Schmal, M.A. Vannice, *J. Catal.* 160 (1996) 106.
- [14] US Patent 4456775 (1984).
- [15] Ch. Travers, J.P. Bournonville, G. Martino, in: *Proceedings of the 8th International Congress on Catalysis*, Vol. 4, Berlin, 1984, p. 891.
- [16] J. Margitfalvi, M. Hegedüs, S. Göbölös, E. Kern-Tálas, P. Szedlacsek, S. Szabó, F. Nagy, in: *Proceedings of the 8th International Congress on Catalysis*, Vol. 4, Berlin, 1984, p. 903.
- [17] US Patent 4628130 (1986).
- [18] O.A. Ferretti, B. de Pauli, J.P. Candy, G. Mabilon, J.P. Bournonville, *Stud. Surf. Sci. Catal.* 31 (1987) 713.
- [19] J.L. Margitfalvi, I. Borbáth, E. Tfirst, A. Tompos, *Catal. Today* 43 (1998) 29.
- [20] B. Didillon, J.P. Candy, F. Lepeltier, O.A. Ferretti, J.M. Basset, *Stud. Surf. Sci. Catal.* 78 (1993) 203.
- [21] B. Didillon, C. Houtman, T. Shay, J.P. Candy, J.M. Basset, *JACS* 115 (1993) 9380.
- [22] J. Margitfalvi, A. Tompos, I. Kolosova, J. Valyon, *J. Catal.* 174 (1998) 246.
- [23] P. Claus, *Top. Catal.* 5 (1998) 51.
- [24] G.F. Santori, M.L. Casella, G.J. Siri, H.R. Adúriz, O.A. Ferretti, *Appl. Catal. A: Gen.* 197 (2000) 141.
- [25] G.F. Santori, M.L. Casella, G.J. Siri, O.A. Ferretti, *Stud. Surf. Sci. Catal.* 130C (2000) 2063.
- [26] C.M. Pradier, Y. Berthier, G. Cordier, J. Oudar, *Stud. Surf. Sci. Catal.* 98 (1991) 505.
- [27] T. Birchem, C.M. Pradier, Y. Berthier, G. Cordier, *J. Catal.* 146 (1994) 503.
- [28] V. Ponec, *Appl. Catal. A: Gen.* 149 (1997) 27.
- [29] F. Delbecq, P. Sautet, *J. Catal.* 152 (1995) 217.
- [30] P. Sautet, *Top. Catal.* 13 (2000) 213.
- [31] G.F. Santori, Ph.D. Thesis, Universidad Nacional de La Plata, 2000.
- [32] G.M.R. van Druten, L. Aksu, V. Ponec, *Appl. Catal. A: Gen.* 149 (1997) 181.
- [33] T. Ohkuma, H. Ooka, T. Ikariya, R. Noyori, *JACS* 117 (1995) 10417.
- [34] R.D. Cortright, J.A. Dumesic, *Appl. Catal. A: Gen.* 129 (1995) 101.
- [35] M. Englisch, V.S. Ranade, J. Lercher, *Appl. Catal. A: Gen.* 163 (1997) 111.
- [36] G.M.R. van Druten, V. Ponec, *Appl. Catal. A: Gen.* 191 (2000) 153.
- [37] U. Singh, M.A. Vannice, *J. Catal.* 191 (2000) 165.
- [38] U. Singh, M.N. Sysak, M.A. Vannice, *J. Catal.* 191 (2000) 181.
- [39] R.M. Makouangou, D.Y. Murzin, A.E. Dauscher, R.A. Touroude, *Ind. Eng. Chem. Res.* 33 (1994) 1881.
- [40] J.L. Margitfalvi, Gy. Vankó, I. Borbáth, A. Tompos, A. Vértes, *J. Catal.* 190 (2000) 474.