

Hydrogenation of crotonaldehyde on Pt/SiO₂ catalysts modified with tin added via surface organometallic chemistry on metals techniques

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Abstract

The importance of the preparation procedure and the understanding of the mechanisms that control this stage on the final properties of the catalyst are evidenced for PtSn systems obtained via surface organometallic chemistry on metals (SOMC/M) techniques. The temperature of preparation reaction also plays a fundamental role as regards the nature of the active phase finally obtained, giving rise to catalytic phases having different levels of selectivity to unsaturated alcohols (UOL) in the crotonaldehyde hydrogenation. Organobimetallic catalysts lead to very high selectivities to crotyl alcohol (80% at 5% conversion). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Platinum–tin catalysts; Surface organometallic chemistry; Hydrogenation; Crotonaldehyde

1. Introduction

The hydrogenation of carbonyl groups in compounds containing ethylenic bonds for obtaining the corresponding unsaturated alcohols (UOL) is a very important reaction in the field of fine chemicals. Extensive work has been carried out to develop heterogeneous catalysts for these reactions; in most cases, the catalysts are supported metals of group VIII. On transition metals, selective hydrogenation of C=O group is very difficult because the C=C double bond hydrogenation is both thermodynamically and kinetically favored [1,2], mainly for small molecules (acrolein and crotonaldehyde) where additional steric effects are not important. Monometallic systems based on

transition metals readily achieve the hydrogenation reaction leading to saturated aldehydes (SAL), saturated alcohols (SOL), and to a lesser extent, UOL. In order to improve the selectivity towards UOL, diverse alternatives have been studied, such as the use of different supports, the increment of the size of the metallic particles, and the promotion of the metallic phase by the addition of other metals.

The use of supports like TiO₂, where an effect of strong metal–support interaction (SMSI) was observed at high reduction temperature, is one of the recommended routes. It is proposed that TiO_x, having coordinatively unsaturated Ti cations which could interact with the electron pair donor site of C=O bond, facilitates the adsorption of the unsaturated aldehyde, in a favorable way to produce UOL [3,4]. Concerning the metallic phase, both theoretical and experimental studies indicate that larger particles improve the selectivity to UOL. In effect, it was reported that the selec-

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tivity to UOL in crotonaldehyde hydrogenation with Pt/SiO₂ increased from 17 to 40%, whereas the metal dispersion decreased from nearly 100 to 25% [5,6].

A well known alternative is the modification of the monometallic catalyst by addition of other metals like Sn, Fe, Ge, Ga [7–12]; among them, tin is the most employed and it is normally incorporated from inorganic salts. These types of techniques do not assure an efficient control of the bimetallic active phase obtained. XPS studies showed that most of the tin is in ionic state, although some Sn(0) is also observed. A recent study reported that approximately 30% of tin determined by XPS is in the metallic state for PtSn/C catalysts prepared by using H₂PtCl₆ and SnCl₂ precursors with a ratio (Sn/Pt)_{bulk}=1 [13]. Although the effect of tin is not yet completely well understood, it is explained as follows: the Snⁿ⁺ species have a promoting effect by inducing the polarization of the C=O bond, whereas either the probable formation of a PtSn alloy or the dilution of Pt surface atoms by tin would hinder the C=C bond hydrogenation [14–16]. It has been reported in the literature that, for crotonaldehyde hydrogenation with PtSn catalysts supported on SiO₂, Al₂O₃ or C, selectivities to UOL are slightly above 40%.

Numerous routes have been used in the preparation of bimetallic catalysts. One of them is the so-called surface organometallic chemistry on metals (SOMC/M), which provides technical procedures to prepare catalytic systems in a controlled way [17–20]. The catalysts thus obtained present both high activity and selectivity for many reactions in the field of chemicals and fine chemicals [21–25], as it has been shown for solids obtained by modifying Rh/SiO₂ with SnBu₄ which catalyze the hydrogenation of citral to geraniol with a selectivity above 80% [26].

The present work reports the performance of Pt/SiO₂ catalysts modified with tetra-*n*-butyltin in crotonaldehyde hydrogenation. Techniques derived from SOMC/M were employed to incorporate tin, by reacting Pt/SiO₂ catalyst with SnBu₄ in an H₂ atmosphere.

2. Experimental

2.1. Catalyst preparation

A Degussa silica (Aerosil 200, 200 m² g⁻¹) was used as support. The silica was suspended in NH₄OH_(aq) under stirring prior to the addition of the

[Pt(NH₃)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 H₂ at the same temperature, leading to the monometallic Pt/SiO₂ catalyst.

The catalyst preparation consisted of the reaction of a solution of SnBu₄ in a paraffinic solvent (*n*-heptane and *n*-decane, for temperatures below and over 363 K, respectively) with the reduced Pt/SiO₂ catalyst between 363 and 423 K under flowing H₂. After 4 h under reaction, the liquid phase was separated and the solid was repeatedly washed with *n*-heptane and subsequently dried in Ar at 363 K. The solids obtained after this procedure, identified as organobimetallic catalysts (PtSn-OM) still had butyl groups grafted to the surface. The bimetallic phases (PtSn-BM) were obtained by elimination of the organic groups by activation of PtSn-OM catalysts in flowing H₂ at 773 K for 2 h. The variation of SnBu₄ concentration and the quantity of hydrocarbons evolved during the preparation reaction were analyzed using a Varian 3400 CX gas chromatograph equipped with a flame ionization detector, employing an 10% OV-101 column (1/8 in. i.d., 0.5 m length) and a tricresyl phosphate column (1/4 in. and 6 m length), respectively.

2.2. Catalyst characterization

The contents of platinum and tin were determined by atomic absorption. Hydrogen chemisorption was measured in a static volumetric apparatus at ambient temperature. For each sample, 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 adsorption was carried out in the same manner. The difference between the two isotherms extrapolated to zero pressure gave the quantity of the irreversibly adsorbed hydrogen H/Pt. 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. Temperature programmed reduction (TPR) experiments were carried out in a conventional flow reactor equipped with a thermal conductivity detector by flowing $20 \text{ cm}^3 \text{ min}^{-1}$ (10% H_2 in N_2) at a heating rate of 10 K min^{-1} .

XPS analysis were obtained with an ESCA 750 Shimadzu spectrometer equipped with a hemispherical electron analyzer and a Mg $\text{K}\alpha$ (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 samples were dried and PtSn-BM samples were reduced in situ at 673 K for 1 h. The binding energy (BE) of the C1s 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.

2.3. Catalytic tests

The hydrogenation of crotonaldehyde in liquid phase was performed in a batch reactor at atmospheric pressure and 298 K, employing 0.5 g of catalyst. The aldehyde was introduced into the stirred reactor dissolved in isopropyl alcohol. The progress of the reaction was followed by sampling a sufficient number of microsamples. The composition of the samples was analyzed by means of a Varian GC 3400 gas chromatograph, equipped with a 30 m J&W DB-WAX capillary column and a flame ionization detector.

Pt/SiO₂ and PtSn-BM catalysts were pretreated under flowing H_2 , increasing the temperature from ambient to 773 K, and holding it for 2 h. PtSn-OM catalysts were prepared and tested in the same reactor to prevent any contact with the atmosphere.

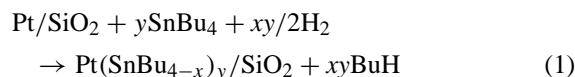
3. Results and discussion

3.1. Preparation of organobimetallic and bimetallic catalysts

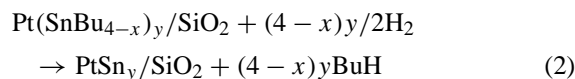
The two-step anchoring process to prepare the PtSn-OM and PtSn-BM catalysts can be represented

by the following reaction scheme:

363–423 K:



423–773 K:



Blank experiments performed on silica via the above-described preparation procedure did not evidence either a variation in the concentration of tetra-*n*-butyltin between 298 and 423 K nor a detectable concentration of tin in the solids. These results are in agreement with a previous work on $\gamma\text{-Al}_2\text{O}_3$ [23].

The reaction between SnBu₄ and Pt/SiO₂ was followed by GC analysis, measuring the variation of SnBu₄ concentration in the impregnating solution and the total quantity of butane evolved per SnBu₄ reacted. The results reported in Figs. 1 and 2 show that: (i) the reaction rate, measured as the amount of SnBu₄ reacted at a given temperature, does not depend on its initial concentration; (ii) an increase in temperature has a beneficial influence on both the SnBu₄ reacted with Pt/SiO₂ and the rate of reaction (1). In fact, at 363 K, it is possible to fix tin selectively onto platinum up to an Sn/Pt ratio of approximately 0.40; whereas it increases to 1.40 when the reaction temperature is 423 K. The apparent activation energy estimated from the initial reaction rate is 55 kJ mol^{-1} .

The data presented in Table 1 indicate that the cleavage of Sn–C bonds and the elimination of butyl groups as butane depend on the amount of SnBu₄ added and on the temperature. When reaction (1) is carried out at 363 K, there is complete removal of butyl groups provided that the Sn/Pt ratio is kept under 0.2 (approximately four BuH evolved per SnBu₄ reacted), while for the plateau (Sn/Pt \cong 0.40), the amount of butane eliminated per fixed tin is next to 2.2, leading to an organobimetallic supported phase with a global stoichiometry Pt(SnBu_{1.8})_{0.4}/SiO₂. For higher temperatures, for example 423 K, reaction (1) proceeds with a complete detachment of butyl groups as BuH, up to an Sn/Pt ratio close to 0.40, whereas for the plateau value (Sn/Pt \cong 1.40), an evolution of approximately 1.3

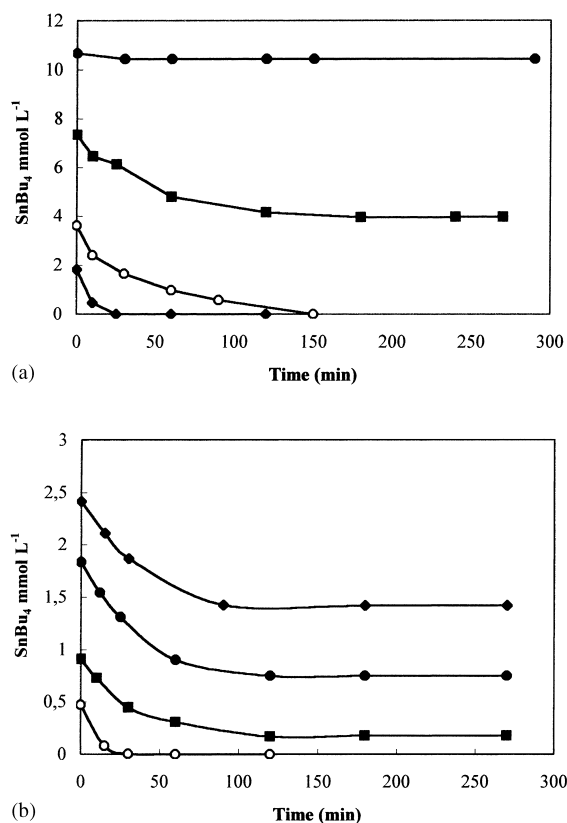


Fig. 1. Variation of SnBu_4 concentration in the impregnation solution (mmol l^{-1}) as a function of time (min). Reaction temperature: (a) 423 K (\circ 3.60 mmol l^{-1} , \blacksquare 7.32 mmol l^{-1} , \blacklozenge 1.81 mmol l^{-1} , \bullet SiO_2); (b) 363 K (\circ 0.47 mmol l^{-1} , \blacksquare 0.91 mmol l^{-1} , \blacklozenge 2.41 mmol l^{-1} , \bullet 1.81 mmol l^{-1}).

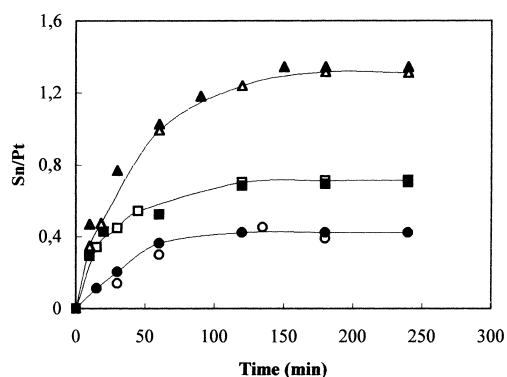


Fig. 2. Amount of tin fixed (measured as Sn/Pt ratio) as a function of time (min) at different temperatures: 363 K (\circ 0.47 mmol l^{-1} , \bullet 2.41 mmol l^{-1}); 393 K (\blacksquare 0.91 mmol l^{-1} , \square 1.81 mmol l^{-1}); 423 K (\blacktriangle 3.60 mmol l^{-1} , \triangle 7.32 mmol l^{-1}).

Table 1
Amount of tin fixed (Sn/Pt ratio) and butane evolved per SnBu_4 reacted (BuH/Sn) at different temperatures

	Temperature							
	363 K		393 K		423 K			
Sn/Pt	0.06	0.12	0.24	0.40	0.70	0.40	0.70	1.40
BuH/Sn	3.8	4.0	2.4	2.2	2.0	3.9	2.4	1.3

butane per fixed tin is observed and the organobimetallic phase so obtained presents a global stoichiometry $\text{Pt}(\text{SnBu}_{2.7})_{1.4}/\text{SiO}_2$.

For the higher temperatures studied, $\text{Sn/Pt}=1.40$ might be attributed to tin-anchored species on the support, formed by migration of activated SnBu_4 molecules from platinum to the metal–support interface, as in the case of the reaction of SnBu_4 with Rh/SiO_2 [27]. In this study, it has been demonstrated by NMR that the compound SiO-Sn-Bu_3 ($\text{Sn/Rh}\cong 1.3$) is formed. The presence of these species, along with the previously mentioned $\text{Pt}(\text{SnBu}_{4-x})_y$ stoichiometry, imply a loss in the control of reaction (1) for temperature higher than 363 K and $\text{Sn/Pt}>0.70$.

According to the observed global stoichiometry, the kinetic curves for $\text{Sn/Pt}<0.70$, shown in Figs. 1 and 2, indicate a reaction mechanism in two stages; a fast first one, where SnBu_4 molecules react with superficial platinum in the presence of hydrogen, causing the hydrogenolysis of Sn-C bonds and the detachment of all the butyl groups as butane, and a second stage, slower, corresponding to the reaction between SnBu_4 molecules with the supported phase, with detachment of approximately one molecule of butane per SnBu_4 reacted. Although it is not possible to distinguish between the formation of either Pt-Sn or Sn-Sn bonds, it seems reasonable to propose the formation of a superficial compound of the type $\text{Pt}_3\text{-Sn-SnBu}_3$, in agreement with the global values shown previously. For example, in the case of 0.40 atoms of tin fixed per platinum atom (i.e., the plateau at 363 K), the existence of that species would be indicating that 0.2 atoms of tin are fixed on the superficial platinum, a figure that is coherent with the value of 0.64 obtained for the dispersion of the monometallic catalyst (Table 2); the rest of the tin is fixed on a phase $\text{Pt}_3\text{-Sn}$, forming Sn-Sn bonds, with detachment of one butyl group. These two stages lead, theoretically, to the global elimination of 2.5 butane molecules per SnBu_4 reacted, a value

Table 2
Characterization of bimetallic catalysts PtSn-BM with different Sn/Pt ratios

Sn/Pt	H/Pt	d_{TEM} (nm)	T_{TPR} (K)	
			Peak 1	Peak 2
0	0.64	2.4	390	700
0.06	0.27	2.7	410	700
0.40	0.20	2.9	430	700

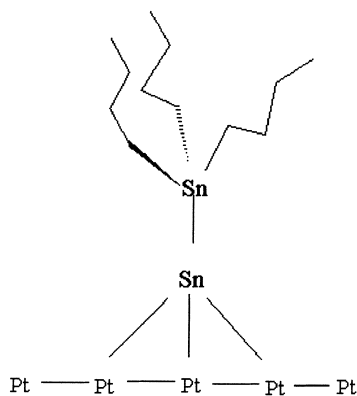
that is in the order of results from Table 1. These data suggest the formation of an organobimetallic supported phase (see Scheme 1), in which tin retains its tetrahedral configuration (as in SnBu_4), just as has been presented in the literature [28].

3.2. TEM, TPR and H_2 chemisorption

The results of the characterization of the studied catalysts by TEM, TPR and H_2 chemisorption are presented in Table 2.

The results of TEM measurements indicate that the particle size distribution of both mono- and bimetallic catalysts are very narrow, with a mean particle diameter around 2.4 nm, for Pt/SiO₂, and with a slight increment of the mean, for PtSn-BM, in the order of approximately 0.3–0.5 nm.

The chemisorption runs reveal, for Pt/SiO₂, a high metal dispersion (H/Pt=0.64) and an important decrease in H/Pt for PtSn-BM as the tin content increases, even for very small quantities of tin added, which might be ascribed to a homogeneous and spe-



Scheme 1. Proposed organobimetallic supported phase formed by reaction between Pt/SiO₂ and SnBu_4 .

Table 3
Binding energies (eV) and surface atomic fraction of Sn(0) for tin modified catalysts^a

Catalyst	Sn/Pt	Binding energies (eV)			$\text{Sn}^0/(\text{Sn}^0+\text{Sn}^{n+})$
		$\text{Sn}^03d_{5/2}$			
		Pt4f _{7/2}	$\text{Sn}^03d_{5/2}$	$\text{Sn}^{n+}3d_{5/2}$	
Pt/SiO ₂	0	71.0	–	–	–
PtSn-BM	0.12	71.1	484.4	486.5	0.75
PtSn-BM	0.24	71.1	484.4	486.5	0.70
PtSn-BM	0.40	71.1	484.4	486.5	0.67
PtSn-BM*	0.40	71.2	484.6	486.5	0.65
PtSn-BM*	0.70	71.2	484.6	486.5	0.64
PtSn-OM	0.40	71.0	484.4	486.5	0.45
PtSn-OM*	0.40	71.0	484.6	486.6	1.00

^a Preparation conditions: catalysts were prepared at 363 K, except those indicated with *, which were obtained at 423 K. The sample PtSn-OM* corresponds to a solid obtained by reaction (1), with no butyl groups attached to the surface (see Table 1).

cific deposition of tin over superficial platinum. Higher tin contents only introduce a slight additional decrease in the chemisorbed hydrogen.

TPR analysis of Pt/SiO₂ reveals the existence of two peaks of hydrogen consumption, as is known from the literature [29]; the first one, centered around 390 K, usually assigned to a platinum oxide having a weak interaction with the support, and the other one around 700 K which corresponds to a platinum oxide with a stronger interaction with the support (probably, a silicate can be formed). PtSn-BM show an increment of the lower temperature peak, indicating an important hydrogen consumption for the reduction of tin oxide, which can be explained in terms of the existence of an important interaction between platinum and tin, platinum being responsible for H_2 dissociation. TPR profiles do not show any peak in the zone corresponding to the reduction of bulk tin oxides, which occurs at temperatures above 900 K [30].

3.3. XPS results

Table 3 gives the position of all the main photoelectron peaks after referencing them to the C1s BE of 284.6 eV. For all the studied catalysts in the region corresponding to Pt4f_{7/2} at 71.1 eV, there appears one peak indicating the complete reduction of platinum. Fig. 3 shows the XPS Sn3d_{5/2} region for both PtSn-BM and PtSn-OM catalysts. For the PtSn-BM series, both Sn(II, IV) and Sn(0) are found at 486.4

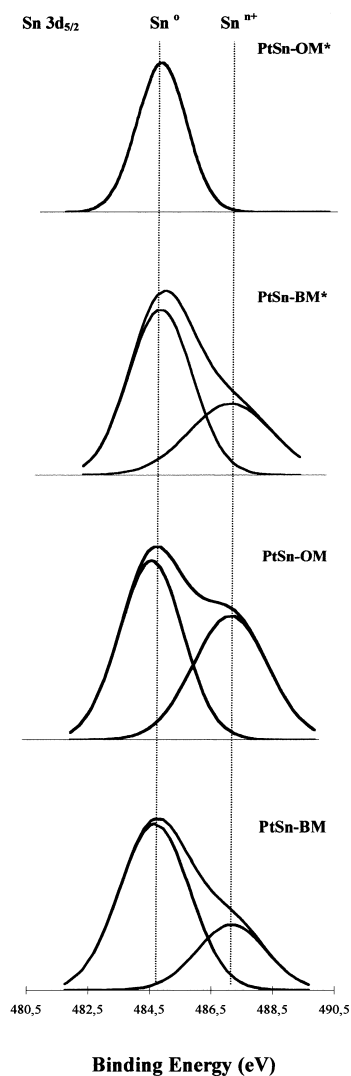


Fig. 3. XPS spectra of Sn $3d_{5/2}$ level for PtSn-OM*, PtSn-BM*, PtSn-OM and PtSn-BM.

and 484.6 eV, respectively. The deconvolution of the spectra allowed to obtain the contribution of these species in each sample, as is shown in Table 3. The fraction of Sn(0) decreases from 75 to 64% as Sn/Pt increases from 0.12 to 0.70. These results differ significantly from those obtained for PtSn bimetallic catalysts prepared by conventional procedures on γ -Al $_2$ O $_3$ or C, for which the fraction of Sn(0) remained below 0.30 [13,31]. The spectra of the organobimetallic catalysts are somewhat different. A peak at 484.6 eV is always observed, indicating the presence of metal-

lic tin. However, whereas in the case of PtSn-OM* (Sn/Pt=0.4, prepared at 423 K), no oxidized tin appears, a peak at BE=486.4 eV in the spectrum of PtSn-OM (Sn/Pt=0.4, prepared at 363 K) is present, representing approximately 50% oxidized tin. As was mentioned previously, the PtSn-OM* is a solid phase without any butyl groups attached, while in PtSn-OM, there are approximately two remaining butyl groups.

From these results, some aspects related to the controlled reaction (1) may be discussed. At the beginning, all the SnBu $_4$ molecules that react onto supported platinum lose their four Bu groups, giving rise to PtSn sites where Sn(0), probably as adatoms, is decorating platinum particles. In this sense, quantum-chemical self-consistent field calculations carried out to analyze the interaction between an SnMe $_4$ molecule and a reduced rhodium cluster showed that the mechanism implies the initial adsorption of alkyltin on rhodium atoms followed by the cleavage of all Sn–C bonds, where the tin atom retains its tetracoordination. The resulting structure is in agreement with a zero oxidation state for the adsorbed tin atoms [28]. A slower second stage takes place leading to an organobimetallic catalyst. The formation of species Pt $_3$ –Sn–SnBu $_3$ could be proposed to occur in this step, which is compatible with the percentage of oxidized tin determined by XPS for PtSn-OM (Table 3).

When the catalysts of OM series are activated in hydrogen at 773 K, they are transformed into bimetallic catalysts (BM series) according to reaction (2). Most probably, a superficial PtSn platinum-rich alloy is formed, with an approximately constant composition, as it is derived from the slight decrease in chemisorbed hydrogen as a function of Sn/Pt. As has been mentioned already, in all BM catalysts, part of tin is in oxidized state, even in the case in which the corresponding OM catalyst has 100% tin in the zerovalent state. In fact, PtSn-BM* (Sn/Pt=0.40, prepared at 423 K) has 35% Sn $^{n+}$, while the corresponding PtSn-OM* does not present Sn $^{n+}$. The presence of tin in oxidized state in BM catalysts could be explained in terms of the migration of tin atoms to form ionic species at the metal support interface.

3.4. Catalytic tests

Catalysts of OM and BM series (Sn/Pt=0.40) and the monometallic Pt/SiO $_2$ were submitted to croton-

Table 4

Reaction rate ($\text{mol g}^{-1} \text{s}^{-1} \times 10^5$) and apparent activation energy (kJ mol^{-1}) for the hydrogenation of crotonaldehyde on Pt/SiO_2 and tin modified catalysts

Catalyst	Reaction rate	Apparent activation energy
Pt	5.28	26
PtSn-OM	7.54	20
PtSn-OM*	19.4	—
PtSn-BM	13.1	19

aldehyde hydrogenation in liquid phase. The reaction products were: butyraldehyde (SAL), crotyl alcohol (UOL), butanol (SOL) and traces of light hydrocarbons.

Table 4 gathers the results of reaction rates and apparent activation energies for the hydrogenation of crotonaldehyde on the studied catalysts. It can be seen that the apparent activation energies are quite similar and

in good agreement with previously published values [12,13,32]. A remarkable result is the increment in the reaction rate of both organobimetallic and bimetallic catalysts compared to the monometallic one, in spite of the decrease in the chemisorbed hydrogen. This fact may be assigned to the presence of a new kind of active site generated by the controlled reaction between SnBu_4 and Pt/SiO_2 .

The conversion of all samples increased linearly as a function of time, indicating a negligible deactivation and an approximately zeroth reaction order for crotonaldehyde.

Fig. 4a–d point out the selectivity behaviour of Pt/SiO_2 , PtSn-OM, PtSn-OM* and PtSn-BM as a function of crotonaldehyde conversion. It is clearly evident that the selectivity to UOL of Pt/SiO_2 ($S_{\text{UOL}} \approx 10\%$) is improved by the addition of tin in the order $\text{PtSn-OM} > \text{PtSn-BM} > \text{PtSn-OM}^*$, in the 5–95

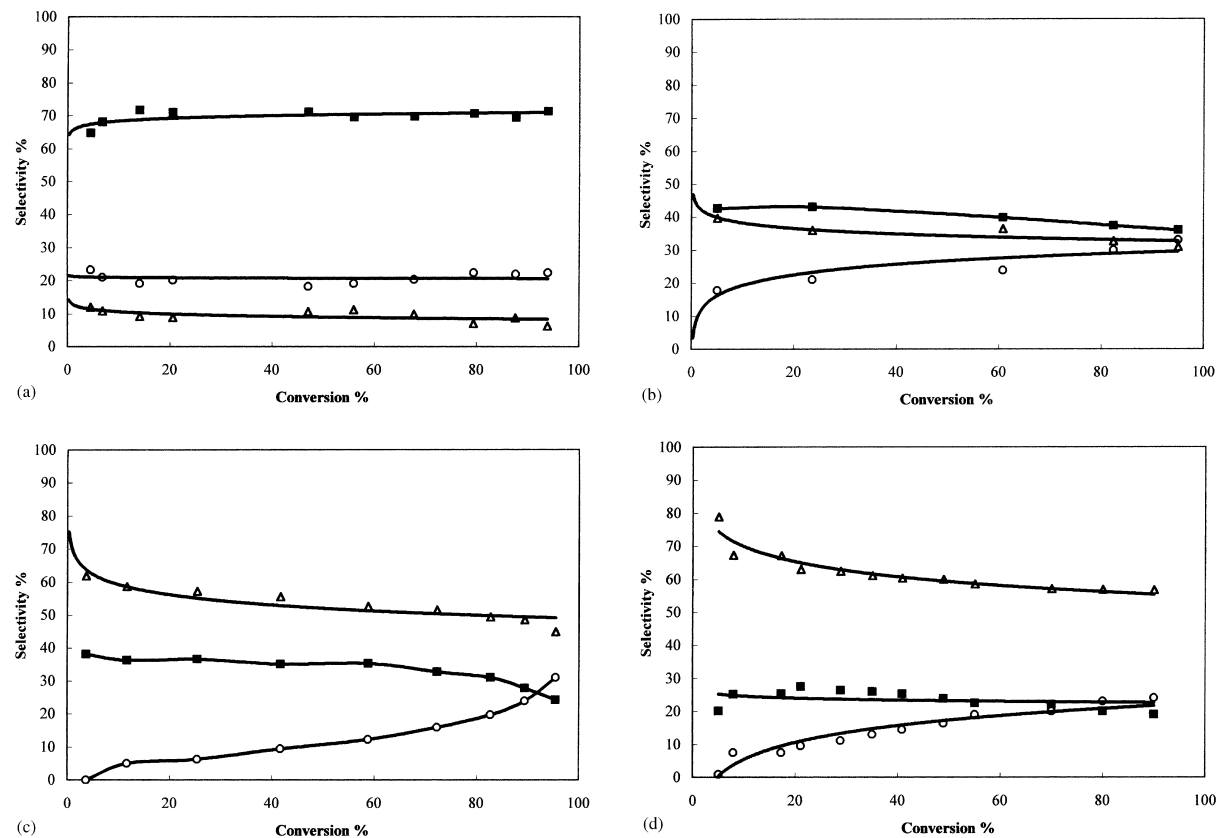


Fig. 4. Selectivities as a function of conversion for (a) Pt/SiO_2 , (b) PtSn-OM, (c) PtSn-BM and (d) PtSn-OM* (for reaction conditions, see the text) (■ SAL; ○ SOL; △ UOL).

conversion range. At 5% conversion, the S_{UOL} values are: 80% (PtSn-OM), 62% (PtSn-BM) and 40% (PtSn-OM*). It is to be noted that the PtSn-OM* sample, in which tin is completely reduced, results in the less selective tin-modified catalyst. For both PtSn-OM and PtSn-BM samples, S_{UOL} presents a slower decrease as a function of conversion. For a conversion level around 90%, S_{UOL} is 60% for PtSn-OM and 48% for PtSn-BM, respectively.

The above-presented selectivity data are in agreement with previous works. The improvement in selectivity might be explained by considering that the ionic tin polarizes the C=O bond in such a way that the attack of hydrogen would be favored with respect to the hydrogenation of olefinic bond. XPS analysis showed that platinum catalysts modified by tin, which present an important contribution of ionic tin, are both more active and selective to UOL. PtSn-OM catalysts prepared from a controlled SOMC/M technique, in which half of tin was in ionic state and approximately two butyl groups were stabilized in the organobimetallic phase, presented the higher selectivity to date for crotyl alcohol on platinum catalysts at atmospheric pressure. This result might be assigned to both electronic and steric effects: electronic, from ionic tin, and steric, due to Bu fragments that facilitate the adsorption of crotonaldehyde through the C=O bond.

4. Conclusions

This work reported on the addition of tin to a Pt/SiO₂ catalyst by using the so-called SOMC/M technique, which generated a very selective Pt–Sn interaction. The results obtained clearly address both the importance of the catalyst preparation procedure to improve the activity/selectivity and the need to understand the mechanism that controls the final properties of the catalysts. At 363 K, an organobimetallic phase is obtained, for which a Pt₃–Sn–SnBu₃ stoichiometry is proposed. In this phase, tin is found both in oxidized and metallic states in similar proportions; however, for higher temperatures (for instance, 423 K) and the same Sn/Pt ratio, all the organic groups are detached from the surface and tin is 100% in the zerothvalent state (probably as an adatom, forming a superficial Pt₃Sn–H compound). The activation in hydrogen at higher temperatures leads to bimetallic

systems, where tin is found mainly in the zerothvalent state (forming superficial alloys with platinum), although oxidized tin is always observed (probably located in the interface with the support). The proportion of oxidized tin increases with the concentration of tin in the catalyst.

Discarding important changes in the size of metallic particles, as well as any effect of the support of the SMSI type, the modifications observed in the catalytic properties are clearly assignable to the effect of tin and the way in which it modifies platinum. In every case, tin improved the activity level of the catalysts, and specially the selectivity towards UOL, even for the system in which it is found 100% as Sn(0) (PtSn-OM*). This fact is indicative of a change in the nature of the active site.

PtSn-OM (Sn/Pt=0.4) catalyst, in which the active phase presents stable organic groups attached to the surface and tin is both as oxidized and metallic species, presents exceptional levels of selectivity, not reported previously for PtSn/SiO₂ catalysts in the hydrogenation of crotonaldehyde at atmospheric pressure. The behaviour of this system may be explained on the basis of a combined effect: the presence of tin in oxidized state leads to a more appropriate polarization of the C=O bond, and the alkyl groups favor sterically the adsorption of the carbonyl group. The bimetallic PtSn-BM catalyst obtained after the activation step (in which part of the tin is in oxidized state) also gives rise to important selectivity values towards UOL, although always below the PtSn-OM catalyst.

Finally, the importance of setting the appropriate experimental conditions for the preparation of these catalysts employing techniques derived from SOMC/M can be remarked on, just as it is put in evidence from the different catalytic properties observed for PtSn-OM and PtSn-OM*. These two catalysts were prepared starting from the same precursor compounds in the same concentration (Sn/Pt=0.4), and the only difference was the temperature at which the experimental procedure was held.

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TEM measurements were performed at CRIBABB, Bahía Blanca (Argentina).

References

- [1] P. Rylander, *Catalytic Hydrogenation over Platinum Metals*, Academic Press, New York, 1967.
- [2] C.L. Thomas, *Catalytic Processes and Proven Catalysts*, Academic Press, New York, 1990.
- [3] M.A. Vannice, B. Sen, *J. Catal.* 115 (1989) 65.
- [4] M.A. Vannice, *J. Mol. Catal.* 59 (1990) 165.
- [5] F. Delbecq, P. Sautet, *J. Catal.* 152 (1995) 217.
- [6] M. Englisch, A. Jentys, J. Lercher, *J. Catal.* 166 (1997) 25.
- [7] Z. Poltarzewski, S. Galvagno, R. Pietrapolo, P. Staiti, *J. Catal.* 102 (1986) 190.
- [8] D. Goupil, P. Fouilloux, R. Maurel, *React. Kinet. Catal. Lett.* 35 (1987) 185.
- [9] D. Richard, P. Fouilloux, P. Gallezot, in: M.J. Phillips, M. Ternan (Eds.), *Proc. 9th Int. Congr. on Catalysis*, Calgary, Vol. 3, 1988, p. 1074.
- [10] D. Richard, J. Ockelford, A. Giroir-Fendler, P. Gallezot, *Catal. Lett.* 3 (1989) 53.
- [11] P. Gallezot, A. Giroir-Fendler, D. Richard, in: W. Pascoe (Ed.), *Catalysis of Organic Reactions*, Dekker, New York, 1991.
- [12] C.G. Raab, M. Englisch, T.B.L.W. Marinelli, J.A. Lercher, *Stud. Surf. Sci. Catal.* 78 (1993) 211.
- [13] F. Coloma, A. Sepúlveda-Escribano, J.L.G. Fierro, F. Rodríguez-Reinoso, *Appl. Catal. A: Gen.* 136 (1996) 231.
- [14] B. Coq, F. Figueras, C. Moreau, P. Moreau, M. Warawdekar, *Catal. Lett.* 22 (1993) 189.
- [15] S. Galvagno, C. Milone, A. Donato, G. Neri, R. Pietrapolo, *Catal. Lett.* 17 (1993) 55.
- [16] P. Kluson, L. Cervený, *Appl. Catal. A* 128 (1995) 13.
- [17] Ch. Travers, J.P. Bournonville, G. Martino, in: *Proc. 8th Int. Congr. on Catalysis*, Berlin, Vol. 4, Verlag-Chemie, Berlin, 1984, p. 891.
- [18] J. Margitfalvi, M. Hegedüs, S. Göbölös, E. Kern-Tálas, P. Szedlacsek, S. Szabó, S. Nagy, in: *Proc. 8th Int. Congr. on Catalysis*, Berlin, Vol. 4, Verlag-Chemie, Berlin, 1984, p. 903.
- [19] O.A. Ferretti, L. Bettega de Pauli, J.P. Candy, G. Mabilon, J.P. Bournonville, *Stud. Surf. Sci. Catal.* 31 (1987) 713.
- [20] J.P. Candy, O.A. Ferretti, J.P. Bournonville, A. El Mansour, J.M. Basset, G. Martino, *J. Catal.* 112 (1988) 210.
- [21] O.A. Ferretti, J.P. Bournonville, G. Mabilon, G. Martino, J.P. Candy, J.M. Basset, *J. Mol. Catal.* 67 (1991) 283.
- [22] O.A. Ferretti, M.L. Casella, *Lat. Am. Appl. Res.* 25 (1995) 125.
- [23] G.J. Siri, M.L. Casella, G.F. Santori, O.A. Ferretti, *Ind. Eng. Chem. Res.* 36 (1997) 4821.
- [24] O.A. Ferretti, G.J. Siri, F. Humblot, J.P. Candy, B. Didillon, J.M. Basset, *React. Kinet. Catal. Lett.* 63 (1998) 115.
- [25] P. Claus, *Top. Catal.* 5 (1998) 51.
- [26] B. Didillon, J.P. Candy, F. Lepeltier, O.A. Ferretti, J.M. Basset, *Stud. Surf. Sci. Catal.* 78 (1993) 205.
- [27] O.A. Ferretti, Ch. Lucas, J.P. Candy, B. Didillon, F. Lepeltier, J.M. Basset, *J. Mol. Catal.* 103 (1995) 125.
- [28] A.H. Jubert, M.C. Michelini, G.L. Estiú, O.A. Ferretti, *Catal. Lett.* 46 (1997) 241.
- [29] E. Merlen, P. Beccat, J.C. Bertolini, F. Delichere, N. Zanier, B. Didillon, *J. Catal.* 159 (1996) 178.
- [30] O.A. Ferretti, Ph.D. Thesis, University of Paris VI, Paris, 1986.
- [31] M.L. Casella, G.J. Siri, G.F. Santori, O.A. Ferretti, M.M. Ramírez, in: *Proc. TOCAT 3*, Tokyo, Vol. 1, 1998, p. 308.
- [32] C.G. Raab, J.A. Lercher, *Catal. Lett.* 18 (1993) 99.