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Silica-supported PtSn Catalysts Obtained Through Surface Organometallic Chemistry on Metals Techniques Using a Hydrosoluble Organotin Promoter. Application to the Selective Hydrogenation of α, β-Unsaturated Aldehydes and Ketones

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Abstract: In this paper we propose the preparation of a PtSn bimetallic catalyst through techniques derived from Surface Organometallic Chemistry on Metals (SOMC/M) using water as solvent. The system, PtSn0.2*ac*, was employed in the chemoselective liquid-phase hydrogenation of acetophenone, cinnamaldehyde and benzaldehyde. The results were compared with those obtained with a PtSn catalyst also prepared *via* SOMC/M, but using a conventional paraffinic solvent.

The aqueous medium-prepared catalyst resulted to be as active in and selective to the desired product (unsaturated alcohols) as that obtained from *n*-heptane. This catalyst has the advantage of being prepared in a solvent compatible with the environment, without losing the superior characteristics of SOMC/M-based systems.

Keywords: PtSn catalysts, SOMC/M, Hydrosoluble organotin promoter, Acetophenone, Cinnamaldehyde, Chemoselective hydrogenation.

INTRODUCTION

The reduction of α,β-unsaturated aldehydes and ketones leads to the production of alcohols used as intermediates in the production of compounds of interest in fine chemistry [1,2]. The catalytic hydrogenation of unsaturated carbonyl compounds is relatively simple with respect to the C=C bond, due to the well-known fact that its hydrogenation is thermodynamically favored. However, the desired product from these reactions is generally the unsaturated alcohol. Due to this fact, the design of catalysts having the ability of inhibiting the hydrogenation of the C=C bond and/or favoring the hydrogenation of the C=O group remains an issue of permanent interest. Most reports found in the literature for the hydrogenation of unsaturated carbonyl compounds are based on catalysts involving metals of 8, 9, 10 or 11 groups (mostly of the Pt group), modified with a more electropositive metal, generating a bimetallic system [2, 3]. The second metal may exist as adatom, forming an alloy, partially oxidized or in ionic state. The difference in electronegativity between the two metals may favor the polarization of the carbonyl bond causing high selectivities to unsaturated alcohols. In some systems, bimetallic geometric effects caused by the presence of the second metal have also been observed [2]. Thus, the addition of a second metal may lead to variations in the activity and/or selectivity of the catalytic system, either through electronic interactions with the first metal or by modifying the architecture of the active site.

There are different strategies for obtaining bimetallic systems [4]. The classical methods of preparation of supported bimetallic catalysts consist of co-impregnation or successive impregnation of the metal precursors, usually incorporated under the form of inorganic salts on the solid support. Despite their simplicity, these techniques have the disadvantage of being difficult to control in terms of the formation of the bimetallic phase, with different metallic compositions coexisting and being, therefore, poorly reproducible. An alternative route for preparing bimetallic catalysts is derived from Surface Organometallic Chemistry on Metals (SOMC/M) techniques. The use of these experimental procedures allows the preparation of controlled catalytic phases by means of the reaction of a supported transition metal, M, (M = Pt, Rh, Ru, Ni, Pd; support = (SiO_2, Al_2O_3) with an organometallic compound of the type $M'R_n$ (M'= Sn, Pb, Ge, Sb; R = Me, Et, Bu, n = 3,4). The strong and specific interactions achieved with SOMC/M techniques lead to catalytic systems with well-defined properties that exhibit better activity and selectivity than the catalysts prepared by conventional methods [5 and references therein].

The preparation of catalysts through SOMC/M techniques involves a surface reaction between the previously reduced base metal and a solution of the organometallic compound. Traditionally, paraffinic solvents are used in the preparation of catalysts. In our research group, we have extensive experience in the preparation of bimetallic catalysts based on Pt, Rh and Ni modified with $Sn(C_4H_9)_4$ using *n*-heptane or *n*-decane as solvent. The resulting systems proved to be active and selective in a wide range of hydrogenation reactions of interest in the fine chemistry field [3, 6-8].

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In order to use more environmentally friendly solvents, in this paper we propose the preparation of PtSn bimetallic catalysts employing SOMC/M techniques in water. In order to do so, the techniques used to achieve the surface reaction between the base metal and the modifier had to be adapted. A water-soluble organometallic compound that has been reported in the literature for the preparation of catalysts via SOMC/M is Bu_3SnOH; however, so far its use has been very limited [9].

The catalytic properties of the resulting bimetallic catalysts are tested in the chemoselective hydrogenation of acetophenone, benzaldehyde and cinnamaldehyde. The results are compared with those obtained with PtSn catalysts prepared *via* SOMC/M techniques, but using conventional paraffinic solvents.

MATERIALS AND METHODS

Monometallic Catalyst Preparation

A platinum monometallic catalyst was prepared by the ion-exchange procedure, using SiO_2 (Evonik, 180 m^2g^{-1}) as support. Prior to its use, silica was treated with aqueous ammonia solution. Then, the solid was contacted with an aqueous solution of the metal precursor $[Pt(NH_3)_4]Cl_2$ (Aldrich) having an appropriate concentration to get 1wt.% Pt in the final catalyst. After 24 h of contact at 25°C, the solid was separated from the solution by vacuum filtration, washed several times, dried at 105°C and finally calcined (500°C for 2 h) and reduced under H_2 flow (500°C for 2 h).

Preparation of Bimetallic Catalysts in Aqueous Media

With the aim of adapting the conventionally used SOMC/M techniques to an environmentally compatible solvent (H_2O), a water-soluble organotin modifier, tributyltin hydroxide (Bu_3SnOH), was used. This compound is not commercially available, so it was synthesized through the hydrolysis of tributyltin acetate ($Bu_3SnOOCCH_3$) (Aldrich) in a KOH solution of pH = 10, following a reference procedure [9,10].

To carry out this reaction, 51 mg of the solid reactant $Bu_3SnOOCCH_3$ was weighed, dissolved in 10 mL of KOH solution (pH = 10) and heated to reflux for 6 h under constant stirring. Once cooled down to room temperature, the aqueous solution of the desired product (Bu_3SnOH) was contacted with 0.25 g of the Pt/SiO_2 catalyst (previously reduced in H_2 flow for 2 h at 500°C) in N_2 flow. The surface reaction between the organotin promoter and the monometallic catalyst was conducted in flowing H_2 at 90°C for 4 h, according to SOMC/M standard procedures. Subsequently, the obtained solid was repeatedly washed with distilled water, under N_2 flow, dried at 105°C and then reduced in flowing H_2 at 500°C for 2 h. These systems are referred to as PtSn0.2*ac*.

Preparation of Bimetallic Catalysts in Paraffinic Solvent

For the preparation of the bimetallic catalyst (PtSn0.2) using conventional organic solvents, the previously reduced monometallic catalyst was reacted with a $SnBu_4$ solution using *n*-heptane as solvent, following well-established preparation procedures [3]. The reaction was carried out in H_2 flow for 4 h at 90°C and, after the reaction had finished, the solid was repeatedly washed with *n*-heptane under N_2 flow and finally, it was treated in H_2 at 500°C for 2 h.

Catalyst Characterization

The platinum loading of the monometallic catalyst was determined by atomic absorption spectroscopy using a Varian Spectra AA 55 instrument. The temperature-programmed reduction (TPR) was performed on a Quantachrome instrument equipped with a thermal conductivity detector. The experiments were performed between RT and 800ºC (10ºC min^{-1}) in a flow of a N_2/H_2 mixture (25 cm^3 min^{-1}) containing 5 vol% of H_2. H_2 and CO chemisorption was conducted in an RXM-100 catalyst characterization instrument (Advanced Scientific Designs Inc., USA).

The tin content of the bimetallic catalysts was determined by chromatographic analysis of the tetra *n*-butyl tin solution, as the difference between its initial and final concentration, using a Varian CP-3800 gas chromatograph, equipped with a capillary column FactorFour CP8907 (VF-1 ms, 15 m x 0.25 mm ID, DF = 0.25) and a flame ionization detector (FID). These results were confirmed by spectrophotometric measurements using phenylfluorone [11]. A good agreement was found between both methods.

The metal particle size distribution was determined in a JEOL 100 Cx Transmission Electronic Microscope. Prior to the analysis 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.

X-ray photoelectron spectra (XPS) were acquired with a multitechnique system (SPECS) equipped with an Al-Kα 100W X-ray source and a hemispherical electron analyzer PHOIBOS 150, operated in fixed analyzer transmission (FAT) mode. The spectra were collected at an energy pass of 30 eV. The powder samples were pressed to form a disk and mounted onto a manipulator that allowed the transfer from the pretreatment chamber to the analysis chamber. In the pretreatment chamber, the samples were reduced for 1 h at 400ºC in flowing H_2. The spectra were recorded once the pressure in the analysis chamber reached a residual pressure of less than 5×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.6 eV. The intensities were estimated by calculating the integral of each peak after subtracting the S-shaped background and fitting the experimental peak to a Lorentzian/Gaussian mix of variable proportion, using the Casa XPS program (Casa Software Ltd., UK).

The Fourier transforms infrared spectra (FT-IR) of the $Bu_3SnCOOCH_3$ (solid) were recorded using a Thermo Nicolet Avatar 370DTGS apparatus, using pressed disks of the solid diluted in KBr. The liquid sample containing the Bu_3SnOH was examined as a film and the spectra of both of them were obtained in the range between 400 and 4000 cm^{-1}.

Hydrogenation of Acetophenone, Benzaldehyde and Cinnamaldehyde

The liquid-phase hydrogenation of the three selected substrates was performed in an autoclave-type reactor (Autoclave Engineers) at 80°C and 10 atm of H_2 pressure, using

Table 1. Chemical composition, mean particle size and hydrogen chemisorption of silica-supported Pt, PtSn0.2 and PtSn0.2*ac* catalysts.

Catalyst	Pt (wt.%)	Sn/Pt (at/at)[a]	d_p (nm)[b]	H/Pt
Pt	1	--	2.0	0.65
PtSn0.2	1	0.2	1.8	0.25
PtSn0.2*ac*	1	0.2	2.0	--

[a] Determined by GC and spectrophotometry
[b] Measured by TEM

0.25 g of catalyst. In each run, 60 mL of 0.07 M solution of the reagents to be hydrogenated was used. The reduction of acetophenone and benzaldehyde was carried out using 2-propanol as solvent. For the hydrogenation of cinnamaldehyde, toluene was chosen as solvent.

The progress of the reactions was followed by gas chromatography on a Varian CP-3800 gas chromatograph equipped with a capillary column CP wax 52 CB (30 m, 0.3 mm *i.d.*) and a FID detector. The reaction products were identified using a GC/MS Shimadzu QP5050 with a capillary column SUPELCO SPBTM-5 (30 m, 0.25 mm *i.d.*).

To rule out the possibility that the hydrogen atoms were provided by the alcoholic solvent (2-propanol), tests were conducted using the same experimental conditions, but under an N_2 atmosphere.

RESULTS AND DISCUSSION

Preparation and Characterization of the Catalysts

Table **1** shows the metal content, the Sn/Pt atomic ratio and the microscopy results obtained for the catalyst systems studied in this work.

As indicated in the experimental section, the Pt/SiO_2 catalyst (1 wt.% Pt, measured by atomic absorption spectroscopy) was prepared by the ion-exchange technique. This technique allows obtaining reproducible systems with high dispersion (H/Pt = 0.65 and Pt/CO = 0.55) [3, 12, 13]. This last feature is of great importance in the preparation of bimetallic catalysts by the method proposed in this work, SOMC/M techniques. A significant amount of exposed base metal ensures the subsequent surface reaction of the organometallic compound with the surface metal.

TPR tests showed the two characteristic peaks of Pt/SiO_2 systems at 250 and 500°C. The first one is associated with the reduction of oxidized platinum species generated during the calcination of the catalyst, while the second one is assigned to platinum species having a somewhat strong interaction with the support [14].

Aiming to develop a more environmentally friendly method of preparing PtSn catalysts through SOMS/M techniques, the hydrosoluble organotin precursor, tributyltin hydroxide (Bu_3SnOH), was used. This compound was obtained from the hydrolysis of tributyltin acetate ($Bu_3SnOOCCH_3$) in strong alkaline medium (KOH, pH = 10). The following equation represents the reaction involved:

$$Bu_3SnOOCCH_3 + OH^- \longrightarrow Bu_3SnOH + CH_3COO^-$$

In order to confirm the presence of Bu_3SnOH (Fig. **1b**), the product obtained after 6 h of reaction was analyzed by FT-IR, and its spectrum was compared with that of the starting reagent ($Bu_3SnOOCCH_3$) (Fig. **1a**). The spectrum of the reaction product showed the presence of a band characteristic of alcohols at 3300 cm^{-1} corresponding to the O-H stretching, consistent with the presence of the desired product (Bu_3SnOH). Both spectra showed two C-H stretching bands characteristic of the methyl groups (one around 2960 and the other around 2870 cm^{-1}) and the symmetric and asymmetric stretching of the methylene groups (about 2920 and 2850 cm^{-1}), which confirms the presence of alkyl groups (in this case butyl) both in the initial reactant and in the product. Also, for the product, it was observed that the bands at 1076 cm^{-1} (assigned to Sn-O-CO) and 1581 cm^{-1} have virtually disappeared, confirming the formation of Bu_3SnOH.

The synthesized precursor was used for the preparation of bimetallic catalysts through SOMC/M techniques in aqueous medium. The tin content of these systems was determined spectrophotometrically using phenylfluorone and yielded a Sn/Pt atomic ratio of 0.2.

For preparing the bimetallic catalysts, a controlled surface reaction between the previously reduced monometallic catalyst and a solution of the organotin modifier was carried out. The preparation of PtSn systems was conducted using two types of solvent. On the one hand, a traditional system was employed, *i.e.*, $SnBu_4$ dissolved in a paraffinic solvent was used as precursor. On the other hand, the water-soluble modifier Bu_3SnOH was used and the reaction was carried out in aqueous medium. In both cases, SOMC/M-derived techniques were used, which involve the selective reaction of the organometallic compound with the transition metal located at the surface of the monometallic catalyst. The reaction of the organotin compound and the SiO_2-supported platinum catalyst takes place in two steps:

$$Pt/SiO_2 + ySnBu_4 + xy2H_2 \longrightarrow Pt(SnBu_{4-x})_y/SiO_2 + xyBuH$$

$$Pt(SnBu_{4-x})_y/SiO_2 + (4-x)y/2H_2 \longrightarrow PtSn_y/SiO_2 + (4-x)yBuH$$

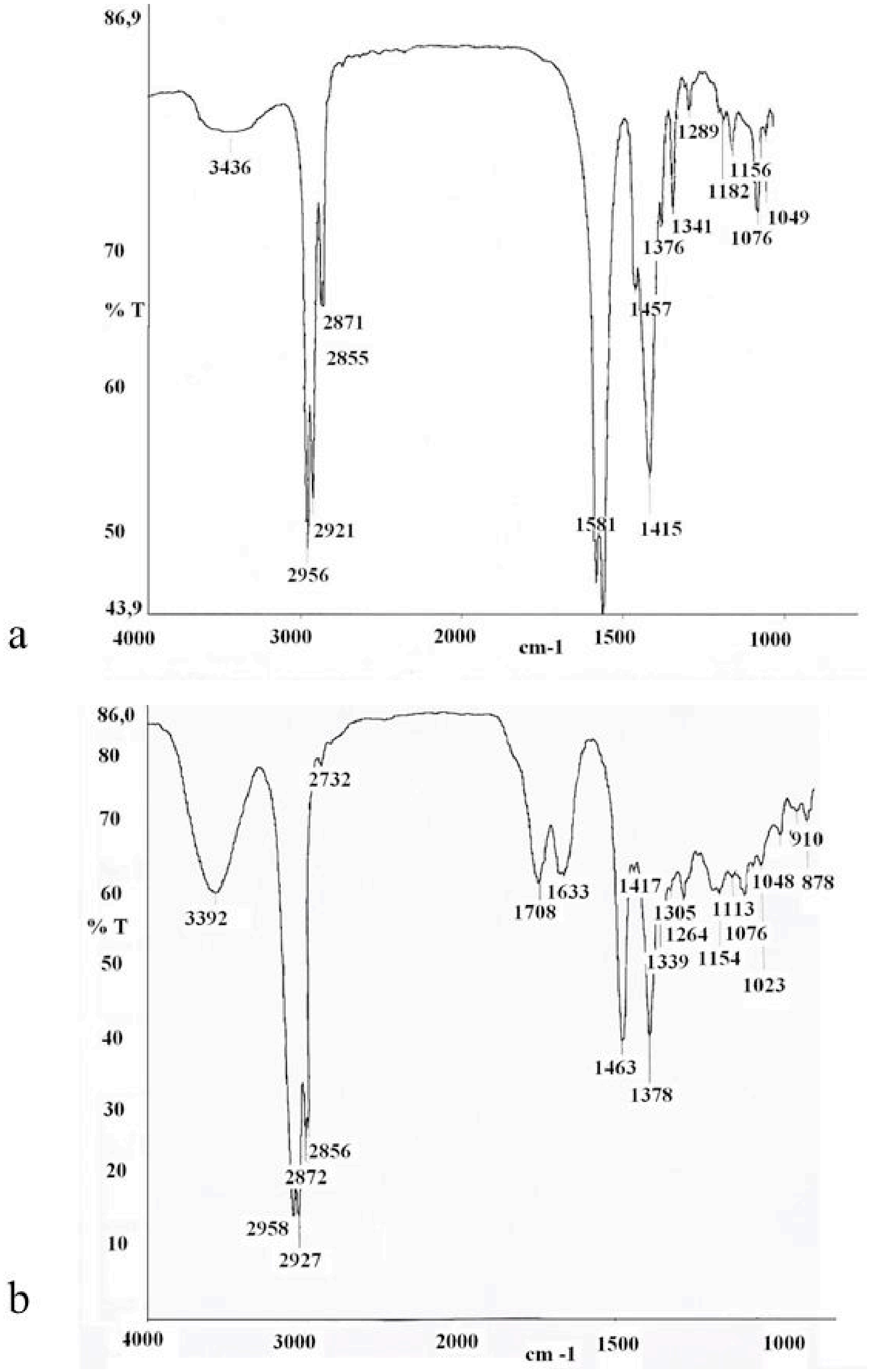


Fig. (1). a- FTIR spectrum of $Bu_3SnOOCCH_3$. b- FTIR spectrum of Bu_3SnOH, the organotin precursor employed in the preparation of PtSn0.2*ac* catalyst.

During the first step (temperature lower than 150°C), catalytic phases with some organic fragments attached to the surface are obtained. In a subsequent step (temperature higher than 150°C), these fragment are eliminated, yielding either bimetallic alloys or adatoms [5]. SOMC/M techniques in aqueous media have not been extensively studied therefore, the mechanism of formation of bimetallic systems is rather unknown, but is expected to behave in steps similar to those above-described for conventional systems.

In order to confirm the specificity of the reactions leading to the bimetallic catalysts, blank experiments were conducted. These tests consisted in reacting $SnBu_4$ and Bu_3SnOH with SiO_2 under the same conditions used for the preparation of the catalysts. It was found that the amount of the tin promoter onto the support was less than 1 wt.%. Similarly, Bentahar *et al.* found no significant reaction between Bu_3SnOH and silica or alumina supports at pH = 10 [8].

Table **1** lists the analysis of the values obtained for the mean particle size. It can be seen that the addition of tin does not practically affect the particle size distribution with respect to the monometallic system. This is an indication of the specificity of the reaction between both metals.

Table 2. **Pt 4f7/2 and Sn 3d5/2 binding energies (BE) and XPS Sn(0)/Sn_{total} and Sn(0)/Pt atomic ratios for Pt, PtSn0.2 and PtSn0.2*ac* catalysts.**

Catalyst	**BE (eV)**		**Sn(0)/Sn_{total}**	**Sn(0)/Pt**
	Pt 4$f_{7/2}$	**Sn 3$d_{5/2}$**		
Pt	71.3	---	--	--
PtSn0.2	71.1	484.1; 486.3	0.55	0.11
PtSn0.2*ac*	69.6	485.5; 486.6	0.46	0.10

*Sn_{total} =Sn(0)+Sn(II,IV)

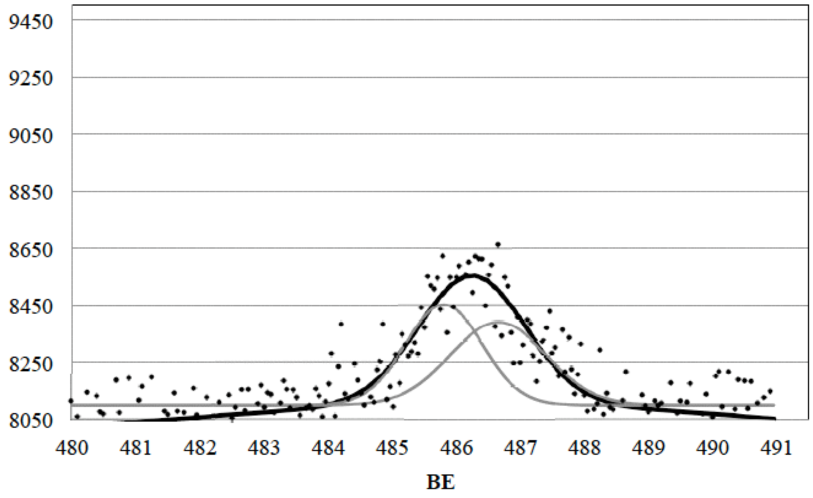
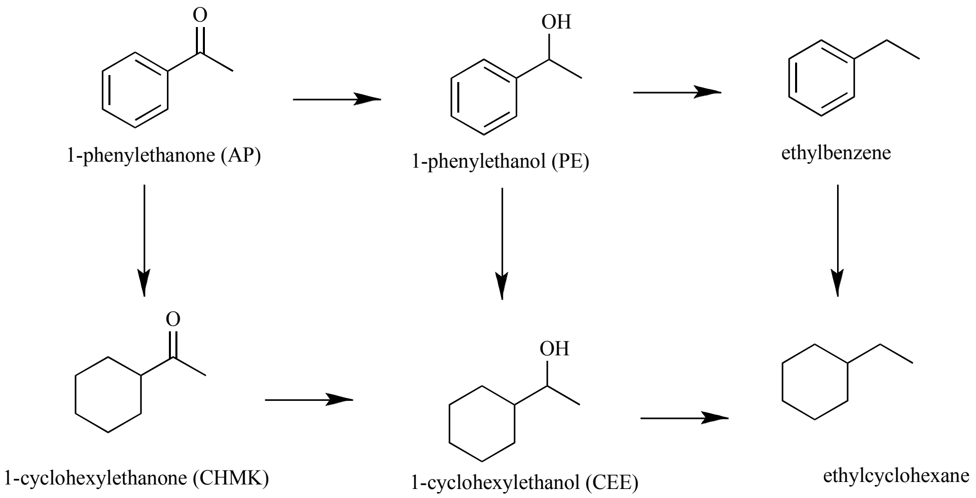


Fig. (2). XPS spectra for the PtSn0.2*ac* (Sn $3d_{5/2}$ level).



Scheme (1). Reaction pathways in the hydrogenation of acetophenone (1-phenylethanone, AP).

In Table **2**, the results obtained from XPS analysis are reported. For all the studied catalysts, the region corresponding to Pt 4*f7/2* (around 71 eV) shows a single peak characteristic of platinum in the metallic state [15]. For both bimetallic catalysts there is a shift of this peak towards lower binding energies (BE), indicative of an electronic effect caused by the addition of tin onto platinum. The spectra of the two bimetallic catalysts present two bands in the region corresponding to Sn 3*d5/2* (Fig. **2**). The lower BE peak corresponds to reduced tin (484.1 and 485.5 eV for PtSn0.2*ac* and PtSn0.2, respectively), while the higher BE peak is attributed to oxidized tin species (Sn (II) and Sn (IV)) (486.3 and 486.6 eV for PtSn0.2 and PtSn0.2*ac*, respectively) [15, 16]. Table **2** also shows the Sn (0)/Pt ratio for both bimetallic systems studied and, as can be seen, this ratio is similar for both catalysts, which would be indicating that the content of reduced tin is similar in both of them.

Hydrogenation of Acetophenone

In Scheme **1** the main products of the hydrogenation of acetophenone are shown. If the C=O double bond is hydro-

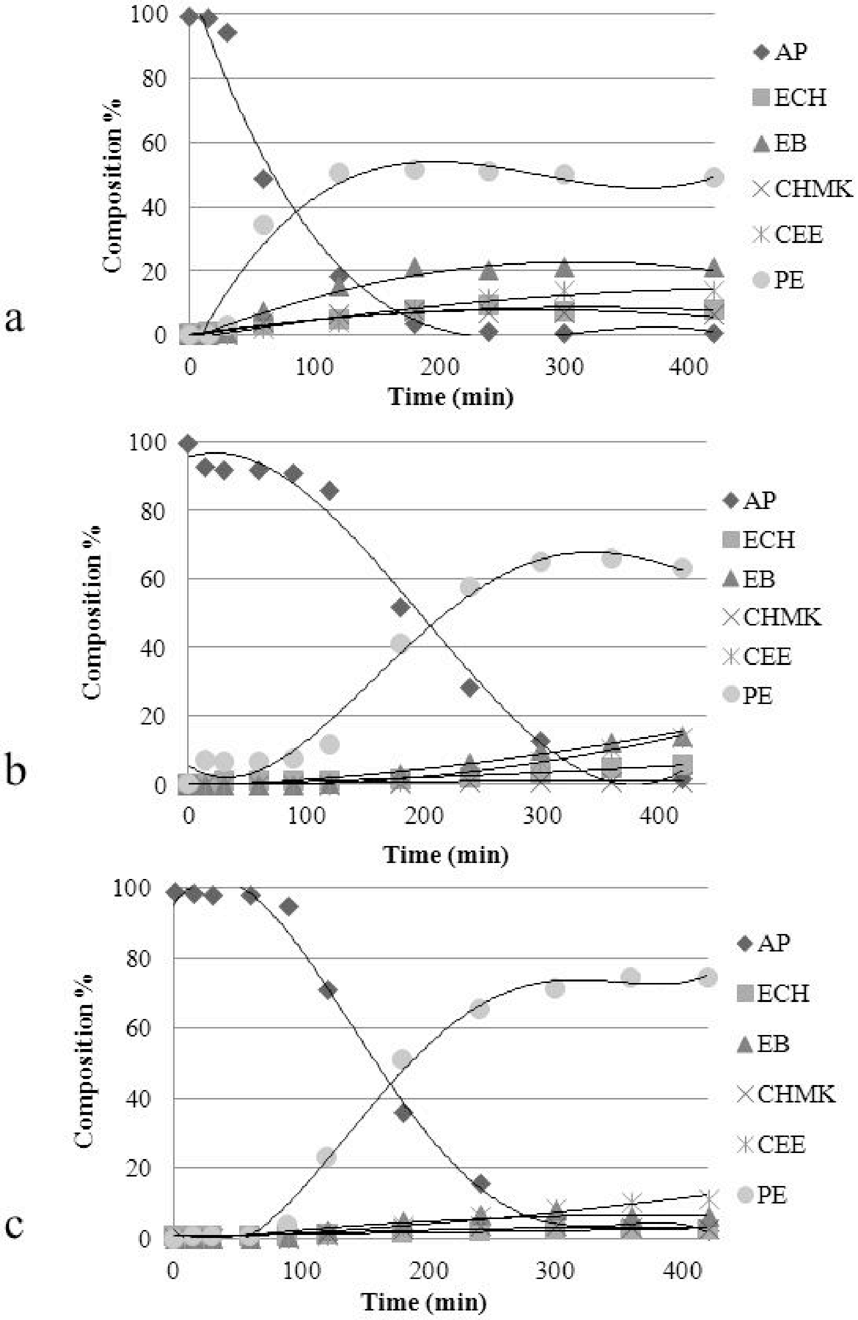


Fig. (3). Product distribution for the selective hydrogenation of acetophenone using (a) Pt, (b) PtSn0.2 and (c) PtSn0.2*ac* catalysts (To understand the meaning of abbreviations, see Scheme **1**).

genated, the desired product, 1-phenylethanol (PE), is obtained. The hydrogenation of the aromatic ring of acetophenone leads to the formation of 1-cyclohexylmethylketone (CHMK), which can be subsequently hydrogenated to obtain cyclohexylethanol (CEE). Alcohols may then originate both ethylbenzene (EB) and ethylcyclohexane (ECH), respectively. The formation of ethylbenzene and ethylcyclohexane can be explained by either the initial hydrogenation of C=O, followed by the dehydration and hydrogen addition to the C=C double bond or by hydrogenolysis of the newly formed C-O bond of the intermediate alcohols [17].

The three employed catalysts (Pt, PtSn0.2*ac* and PtSn0.2) were active in the hydrogenation of acetophenone. For the monometallic one, complete conversion was achieved in 240 min of reaction, whereas for the bimetallic systems, the complete conversion took approximately 420 min. The decrease in activity observed for PtSn0.2*ac* and PtSn0.2 catalysts can be explained by some blockage of the hydrogenation active sites due to the presence of Sn onto Pt particles. These results go in the same direction as other previously reported by our research group [18].

Fig. (**3**) depicts the variation in the composition of reactant and products as a function of reaction time for Pt/SiO$_2$ (Fig. **3a**), PtSn0.2 (Fig. **3b**) and PtSn0.2*ac* (Fig. **3c**) catalysts. For the three of them, the major product is PE. However, for the Pt/SiO$_2$ catalyst the formation of a greater

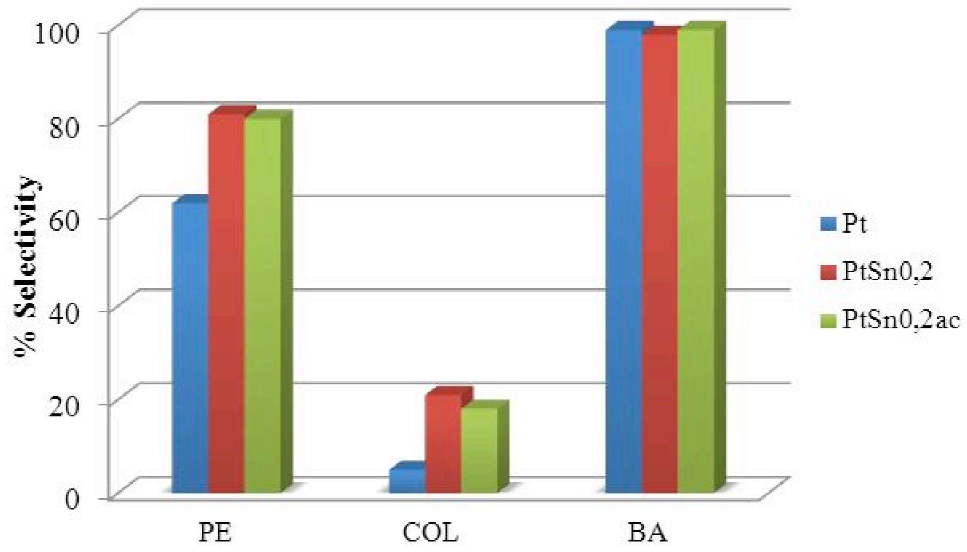


Fig. (4). Selectivity (at 60% conversion) to the desired product (unsaturated alcohol) obtained with the two bimetallic catalysts tested, PtSn0.2 and PtSn0.2*ac* and monometallic Pt/SiO_2: PE (1-phenyl ethanol), COL (cinnamyl alcohol) and BA (benzyl alcohol).

amount of CHMK and of the fully hydrogenated products (EC, EB and ECH) as the reaction proceeds can be observed. From infrared spectroscopy studies reported in the literature, two adsorption modes of acetophenone molecule on a platinum surface are generally accepted. In one of them, the acetophenone molecule is coordinated to the surface through the oxygen of the C=O group, leaving the aromatic ring parallel to the surface and thus promoting its hydrogenation. In the other adsorption mode, the carbonyl group interacts with the surface via the π electron system, so that the aromatic ring remains inclined relative to the surface [19]. Thus, there is a competitive adsorption between the phenyl group and the carbonyl group of the acetophenone molecule. The results found in this work, and others that have already been observed in previous studies, show that for the monometallic system, the adsorption mode leading to the hydrogenation of the aromatic ring would be more favored than in the case of PtSn catalysts [18].

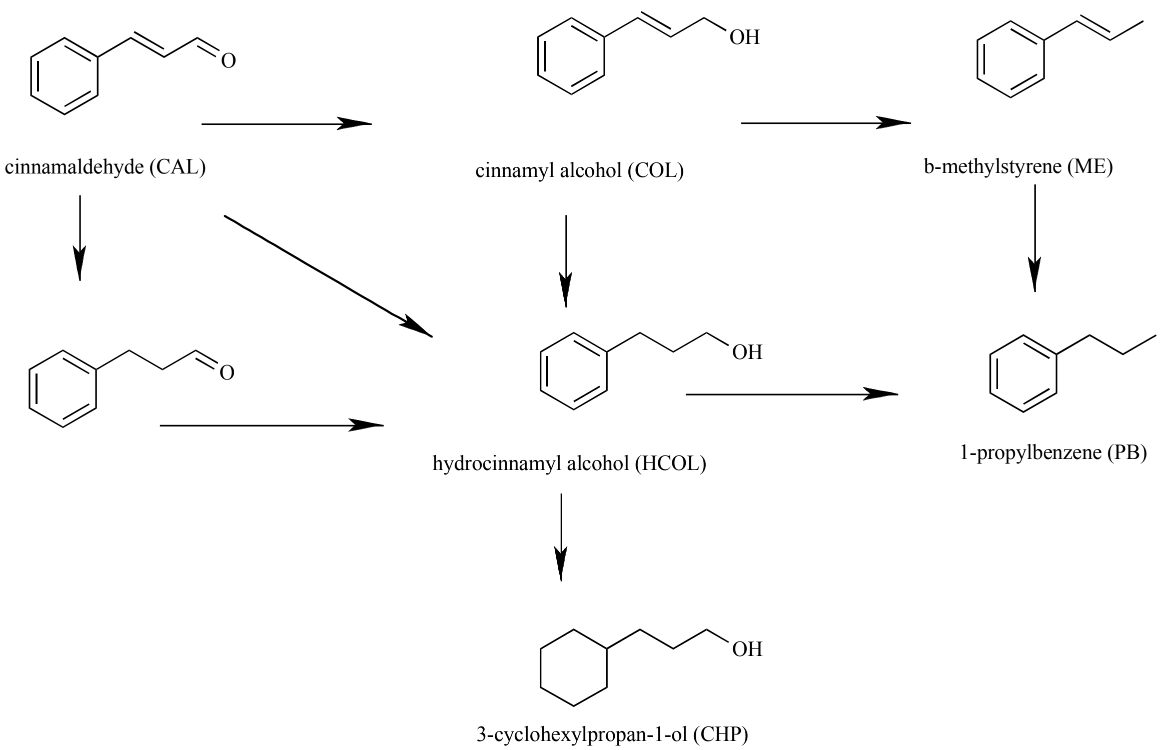
In Fig. (**4**), the selectivity to the desired product (PE) reached with the bimetallic catalysts at 60% conversion is reported. The values obtained were 80% and 81% for PtSn0.2 and PtSn0.2*ac*, respectively. These results mean a significant increase in the selectivity compared to that obtained with the monometallic catalyst (60% for the same conversion value). The presence of Sn, with its electrophilic character, favors the polarization of the carbonyl group, making it more susceptible to the attack of the hydrogen adsorbed on the platinum surface. Furthermore, the presence of tin influences the adsorption mode of the acetophenone molecule through a geometric effect that makes it less likely to be adsorbed in a way in which hydrogen could attack the aromatic ring.

To rule out the possibility that the hydrogen atoms were provided by the alcoholic solvent (2-propanol), hydrogenation tests were conducted using the same experimental conditions, but under an N_2 atmosphere. For over a period of 1 h contact, the formation of acetophenone hydrogenation products was not observed, indicating that the reaction does not proceed by a Meerwein-Ponndorf-Verley type mechanism. After admitting H_2 into the reactor, the hydrogenation of acetophenone started.

Hydrogenation of Cinnamaldehyde

The hydrogenation of cinnamaldehyde is a reaction of importance from a commercial point of view as well as for the research opportunities it provides. Scheme **2** shows all the possible reduction paths for this molecule. The hydrogenation of cinnamaldehyde (CAL) is a process involving the parallel and consecutive reduction of two functional groups, that is, the double C=C and C=O bonds. Generally, a mixture of the desired product, cinnamic alcohol (COL), hydrocinnamaldehyde (HCAL) and hydrocinnamic alcohol (HCOL) is obtained. However, a series of secondary reactions can also take place, which involve the hydrogenation of the aromatic ring, generating 3-cyclohexyl-1-propanol (CHP) and/or hydrogenolysis reactions. In this last case, the presence of β-methylstyrene (MS) and 1-propylbenzene (PB) would indicate a strong adsorption of the hydroxyl group on the metal sites and, therefore, a possible poisoning effect [20].

Fig. (**5**) shows the product selectivity for the three catalysts used. As can be observed, the monometallic Pt/SiO_2 catalyst yielded a greater quantity of HCOL and HCAL, and a very small amount of the desired product, COL. As in the case of acetophenone, the presence of tin promotes the hydrogenation of the carbonyl group and so, higher selectivities of the unsaturated alcohol (COL) can be obtained. According to what is reported in the literature, the cinnamaldehyde molecule adsorption mode leading to the formation of COL is a C=O *atop* geometry. However, DTF calculations conducted by Delbecq and Sautet on adsorption modes of several aldehydes and alcohols on platinum surfaces showed that this adsorption mode is only slightly less favored than the planar adsorption mode through the C=C bond [21]. This fact could let us explain why HCAL is always the major product, even for PtSn systems. The presence of tin results in



Scheme (2). Reaction scheme proposed for the selective hydrogenation of cinnamaldehyde.

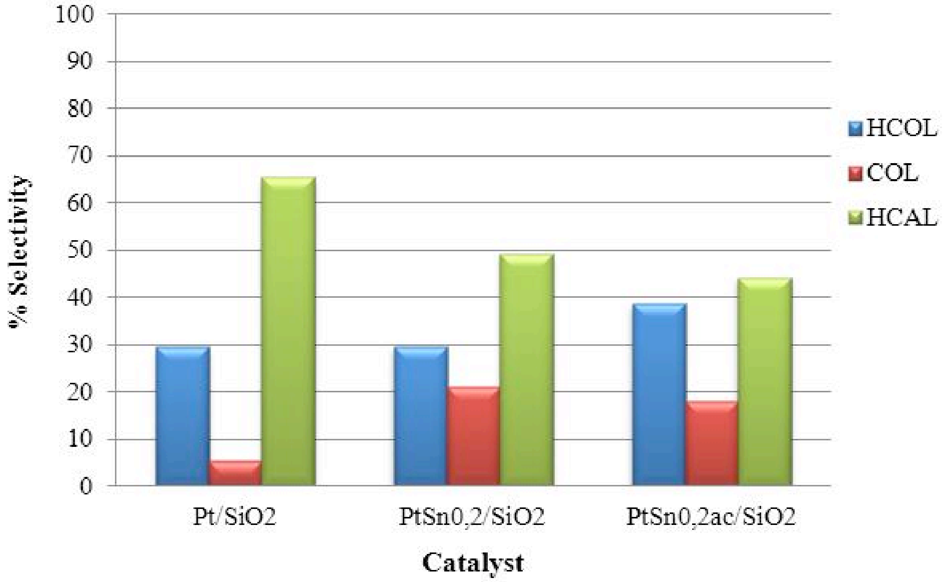


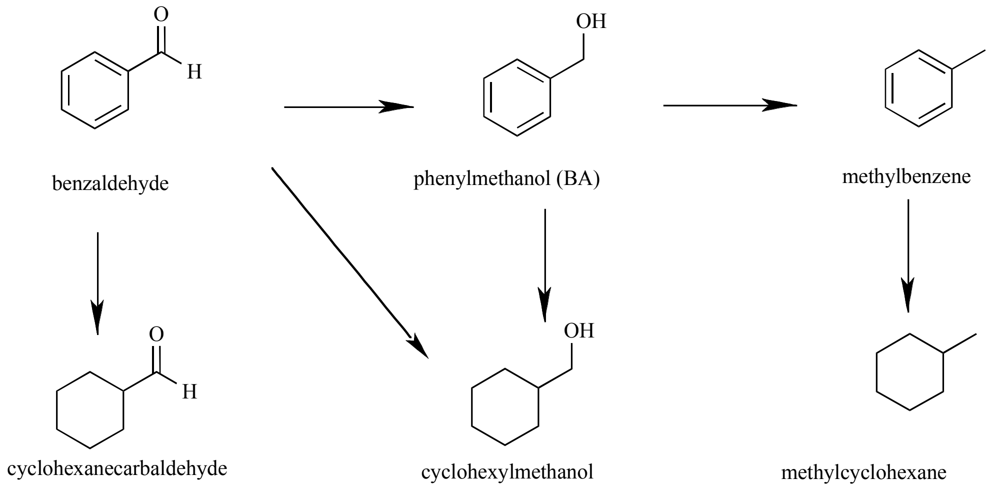
Fig. (5). Effect of the Sn precursor over the selectivity results in the hydrogenation of cinnamaldehyde (at 60% conversion): Pt/SiO_2 (no tin), PtSn0.2 and PtSn0.2*ac* (To understand the meaning of abbreviations, see Scheme **2**).

a partial covering of the platinum surface, which provokes a steric effect increased the hydrogenation of the C=O bond. The most important result is that the selectivity towards COL for the PtSn0.2*ac* prepared in aqueous medium is comparable to that obtained with the system prepared in paraffinic solvent, PtSn0.2 (Fig. **4**).

Concerning the activity observed for the three catalysts, a similar yield was obtained. After 420 min of reaction, a conversion of 69%, 57% and 61% was reached for Pt, PtSn0.2*ac* and PtSn0.2, respectively.

Hydrogenation of Benzaldehyde

In this paper the hydrogenation of benzaldehyde with the three catalytic systems (Pt, PtSn0.2 and PtSn0.2ac) was also studied. In the three cases, benzyl alcohol (BA) was obtained as the sole reaction product, i.e., only the reduction of the carbonyl group took place (Fig. **4**). Scheme **3** depicts the different routes of benzaldehyde hydrogenation that have been reported by other authors [22]. The formation of benzyl alcohol from benzaldehyde occurs *via* a nucleophilic attack on the carbonyl group. To explain this fact, a coplanar ad-



Scheme (3) The hydrogenation path of benzaldehyde.

sorption on the metallic surface of both the aromatic ring and the C=O group is proposed; in this way the polarization of the carbonyl group would be favored and the oxygen would be more susceptible to the nucleophilic attack of hydrogen, thus producing benzyl alcohol almost exclusively. These results agree with which has been published by other authors for benzaldehyde hydrogenation on Au and Pd supported catalysts [22 and references therein].

An interesting fact is that in this study we have not found any etherification product between benzaldehyde and/or benzyl alcohol and the solvent (2-propanol). According to what is reported in the literature, when using ethanol as solvent, the formation of diethyl acetal has been detected [23]. Nor have we observed hydrogenolysis products such as benzene or toluene.

CONCLUSIONS

It has been possible to synthesize and characterize Bu_3SnOH, a hydrosoluble organometallic compound used as catalyst modifier for a silica-supported Pt catalyst. With this compound it has been possible to prepare a bimetallic organotin PtSn system in water *via* Surface Organometallic Chemistry on Metals techniques, PtSn0.2*ac*.

The PtSn0.2*ac* system was tested in the liquid-phase hydrogenation of acetophenone, cinnamaldehyde and benzaldehyde and resulted to be as active in and selective to the desired products (unsaturated alcohols) as that obtained from conventional paraffinic solvents (PtSn0.2). This catalyst has the advantage of being prepared in a solvent compatible with the environment, without losing the superior characteristics of SOMC/M-based systems.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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