

PtSn/SiO₂ catalysts prepared by surface controlled reactions for the selective hydrogenation of cinnamaldehyde

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ABSTRACT

Tin-modified platinum catalysts were prepared by means of a controlled surface reaction, varying the Sn:Pt atomic ratio between 0 and 0.8. The addition of tin caused a noticeable change both in product distribution and the reaction rate. The selectivity to cinnamyl alcohol increases as a function of Sn content, reaching a value of 80% for a Sn:Pt ratio of 0.8. Reaction rate is also higher for bimetallic catalysts than for Pt/SiO₂, with the highest value obtained for systems with Sn:Pt = 0.2–0.4. These results are indicative of the formation of a new type of active sites, compared to those present in the monometallic catalyst. Bimetallic catalysts using a water-soluble tin precursor Bu₃SnOH, were also prepared. An enhanced performance regarding the monometallic catalyst was also obtained with these materials proving to be an environmentally friendlier alternative to obtain PtSn catalysts.

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1. Introduction

The selective hydrogenation of α,β -unsaturated aldehydes to the corresponding allylic alcohols is still a great challenge in heterogeneous catalysis, both from the academic and the industrial point of view [1]. The application of these alcohols often includes processes of the pharmaceutical and cosmetic industries [2], along with several uses as intermediary products in preparative organic synthesis [3]. A typical example is cinnamyl alcohol, which can be obtained from the selective hydrogenation of cinnamaldehyde, and finds applications in the perfumery industry due to its aroma and its fixative properties. It is also an important intermediate in the synthesis of the antibiotic chloromycetin [4].

From a thermodynamic point of view, it is well known that the formation of the saturated aldehyde is favored over that of the unsaturated alcohol. Moreover, it is easier to hydrogenate an isolated C=C bond rather than the C=O from an aldehyde or ketone [5]. As a consequence, considerable efforts have been made in

order to search for a catalytic system able to actively and selectively carry out the preferential hydrogenation of the C=O bond in the presence of a conjugated C=C bond [6,7]. In spite of these difficulties, selectivity towards the unsaturated alcohol can be significantly improved using carefully designed heterogeneous catalysts. The selectivity of the hydrogenation reactions depends on several parameters such as particle size, metal precursor employed, nature of the support, presence of promoters and reaction solvent. The solvent effects on the hydrogenation of α,β -unsaturated aldehydes has been extensively reviewed by Singh and Vannice [8], analyzing factors such as polarity, solubility of hydrogen and substrate–solvent interactions. So far it seems difficult to have a complete description of the so-called “solvent effect”. As an example, a variety of results with respect to solvent polarity has been discussed in the literature. Furthermore, in cinnamaldehyde hydrogenation using polar solvents is known to favor hydrogenation of the C=O bond, whilst with non-polar solvents hydrogenation of the C=C double bond is favored over Pd/C, Pt/C and Co/Al₂O₃ catalysts [9].

When using metal oxides as catalytic supports, there are two main mechanisms concurring to produce high amounts of the unsaturated alcohol: one includes the use of supports with high reducibility (e.g. TiO₂) [10,11], whilst the other involves the addition of metal promoters (e.g. Sn) to yield multi-metallic catalysts [12,13]. Whereas in the first case the mechanism is based on the sub-oxide species migrated from the support to decorate the metal

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surface, the latter takes advantage of an increased electronic interaction between the metals. Among the different combinations, PtSn bimetallic catalysts have been widely studied due to the significant improvement in selectivity results [14–16].

In previous works we studied the hydrogenation of unsaturated carbonyl compounds using various bimetallic PtSn supported catalysts. A significant increase in selectivity towards the unsaturated alcohol was found when the Pt catalysts were modified with Sn introduced using techniques derived from Surface Organometallic Chemistry on Metals (SOMC/M) [17]. This technique involves the reaction between a supported transition metal and an organometallic compound in a H₂ atmosphere allowing control of the various stages of preparation of the catalyst leading to well-defined solid structures with very good catalytic performances [13,18]. In order to extend this methodology for the preparation of catalysts in a more environmentally friendly way, we could examine the use of a water-soluble organometallic tin precursor Bu₃SnOH. This work, reports the preparation of PtSn bimetallic catalysts using SOMC/M techniques. The effect of both, Sn precursor (SnBu₄ and Bu₃SnOH) and its load ($0 < \text{Sn}:\text{Pt} < 1.0$), is investigated in the liquid-phase selective hydrogenation of cinnamaldehyde to cinnamyl alcohol.

2. Experimental

2.1. Catalyst preparation

An Evonik (previously Degussa) silica (Aerosil 200, 180 m² g⁻¹) was used as support to prepare Pt and PtSn catalysts. The pl (isoelectric point) of the SiO₂ is 2, indicating that at pH > 2 the solid surface has mainly negative charges. However, this becomes significant at pH values above 5. Moreover, at pH > 11 occurs an important dissolution of the SiO₂. Therefore, the solid is an excellent cation exchanger at pH between 9 and 11 [19,20].

The catalyst Pt/SiO₂, was obtained by cationic exchange between the support (SiO₂) and the metallic precursor ([Pt(NH₃)₄]Cl₂ Aldrich 99%) in water solution. The support was previously treated with ammoniacal solution (pH = 10.6) for about 30 min. The concentration of the [Pt(NH₃)₄]²⁺ solution was set as to obtain 1 wt.% Pt exchanged on the support. The solid was stirred for 24 h at 25 °C and then it was recovered by filtration from the solution using a vacuum pump. The material was then repeatedly washed with water, dried at 105 °C and reduced in H₂ flow at 500 °C, yielding the monometallic Pt/SiO₂ catalyst.

The bimetallic PtSn/SiO₂ catalysts were prepared according to SOMC/M techniques. A portion of reduced Pt/SiO₂ catalyst was allowed to react with tetrabutyltin (SnBu₄) in a paraffinic solvent. The reaction was carried out in H₂ atmosphere at either 90 °C in *n*-heptane or 120 °C in *n*-decane, depending on the amount of tin to be loaded. After 4 h of reaction, the liquid-phase was separated and the solid was repeatedly washed with *n*-heptane. The material was then dried in N₂ at 90 °C and finally reduced in flowing H₂ at 500 °C for 2 h. The bimetallic catalysts were designated PtSn_y, *y* being the Sn:Pt atomic ratio.

Alternatively, tributyltin hydroxide (Bu₃SnOH) was used as tin precursor in the aqueous phase preparation of the PtSn/SiO₂ bimetallic catalyst. This organometallic precursor was obtained through hydrolysis of tributyltin acetate (Bu₃SnCOOCH₃) at reflux temperature in KOH 0.001 M (pH = 10) for 6 h. Afterwards, the Bu₃SnOH solution reacted with a portion of reduced monometallic catalyst, in flowing H₂ at 90 °C for 4 h. The liquid-phase was separated and the solid was repeatedly washed with water and finally reduced in H₂ at 500 °C for 2 h. These catalysts were designated PtSnA and PtSnB and they have different nominal amounts of tin (Sn/Pt = 1.0 and 0.8 respectively).

2.2. Catalyst characterization

The platinum and tin contents were determined by atomic absorption spectroscopy (Varian Spectra AA55). The tin content of bimetallic catalysts was also analyzed using a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a capillary column FactorFour CP8907 (VF-1 ms, 15 m × 0.25 mm ID, DF = 0.25).

The Fourier transform infrared spectra (FT-IR) of the Bu₃SnCOOCH₃ (solid) was recorded using a Thermo Nicolet Avatar 370DTGS apparatus, using pressed disks of the solid dilutes in KBr. The liquid sample containing the Bu₃SnOH, was examined as a film and both of them were obtained in the range between 400 and 4000 cm⁻¹.

Temperature-programmed reduction (TPR) tests were carried out in a conventional reactor equipped with a thermal conductivity detector with a feeding flow of 25 cm³ min⁻¹ (5% H₂ in N₂) at a heating rate of 10 °C min⁻¹.

H₂ and CO chemisorption measurements were performed in a static volumetric apparatus at ambient temperature (Advanced Scientific Designs Inc., USA).

The size distribution of metallic particles was determined by transmission electron microscopy (TEM) using a JEOL 100 CX 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.

X-ray photoelectron spectra (XPS) were acquired with a multitechnique system (SPECS) equipped with a Al-Kα 100 W 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 disc 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 400 °C in flowing H₂. 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 C 1s 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).

2.3. Cinnamaldehyde hydrogenation

The experimental conditions employed were chosen after checking that the hydrogenations were measured under a kinetic regime, i.e., in the absence of internal and external mass transfer limitations. To do so, several tests with different catalyst masses and stirring rates were investigated.

In a typical test, the liquid-phase hydrogenation of cinnamaldehyde was carried out in a well-stirred stainless steel batch reactor (1000 rpm), the reaction mixture contained *n*-heptane (Aldrich, 99%), 0.14 g cinnamaldehyde (Fluka, 98%), decane (Fluka, 98%, as internal standard for gas chromatography) and 0.20 g of catalyst. Before this mixture was heated to the reaction temperature (90 °C), the solution was first bubbled with nitrogen (under 3 bar pressure) to remove traces of dissolved oxygen. Once the final temperature was reached, hydrogen (also under 3 bar) was used to purge the nitrogen and to pressurize the system to the desired 10 bar. The reaction was then allowed to proceed, and samples were withdrawn to monitor product distribution. The analysis was performed with a DANI GC-1000 gas chromatograph, equipped with a split/splitless injector, a capillary column (WCOT Fused Silica 30 m, 0.32 mm i.d., coated with CP-Sil

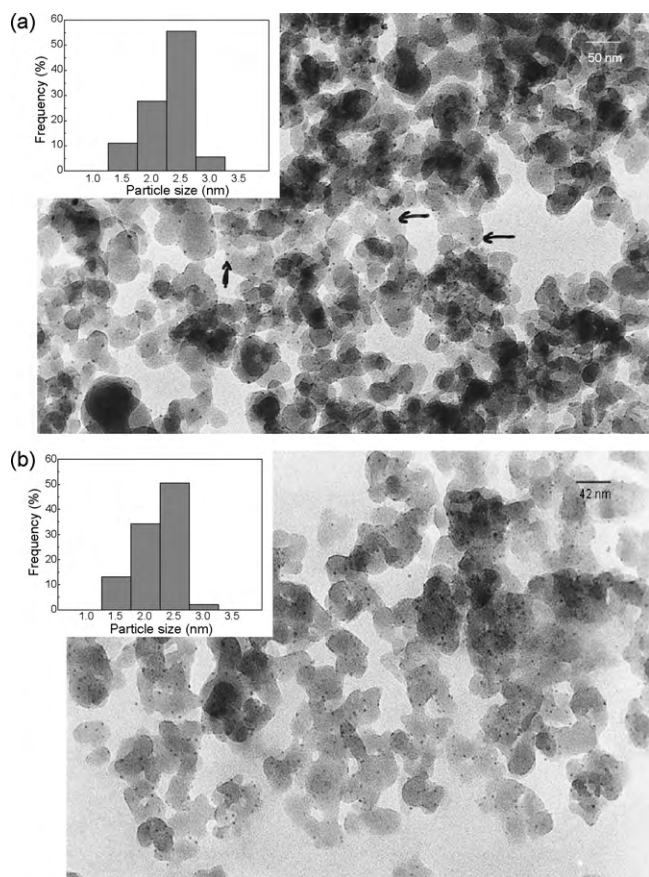


Fig. 1. TEM micrographs and particle size distribution (inset) for (a) Pt/SiO₂ and (b) PtSn_{0.8}/SiO₂.

8 CB low bleed/MS 1 μm film) and a flame ionization detector.

The results of the reaction runs were analyzed in terms of reactant conversion, product selectivity and initial reaction rate as described elsewhere [13,21]. To compare the activity exhibited by the catalysts, the turn-over frequency (TOF) was also calculated.

3. Results and discussion

3.1. Preparation and characterization of catalysts

The TPR spectrum for Pt/SiO₂ catalyst shows two H₂ consumption peaks, one about 254 °C and another at 456 °C. According to the literature, the peak at low temperature is assigned to Pt (IV) species, generated during the calcination pretreatment. On the other hand, the peak at a higher temperature could be assigned to Pt-(O-Si≡)_y^{n-y} (n = 2⁺ or 4⁺) species, formed from the metallic precursor-support interaction [22]. The peaks are wide and have shoulders, which could be due to the environment of the ions on the support surface.

Data obtained from the TPR test allowed us to establish the conditions for activation of the Pt/SiO₂ monometallic catalyst: reduction in H₂ flow at 500 °C for 2 h.

The monometallic Pt/SiO₂ catalyst was prepared using an ionic exchange approach and a material with a relatively high metal dispersion (H/Pt = 0.65, CO/Pt = 0.55) was obtained. Analysis by TEM confirmed the presence of uniform particles with a mean particle size centered at around 2 nm (Fig. 1). In order to prepare bimetallic catalysts by means of SOMC/M techniques it is essential that the noble metal present in the parent material possesses both small

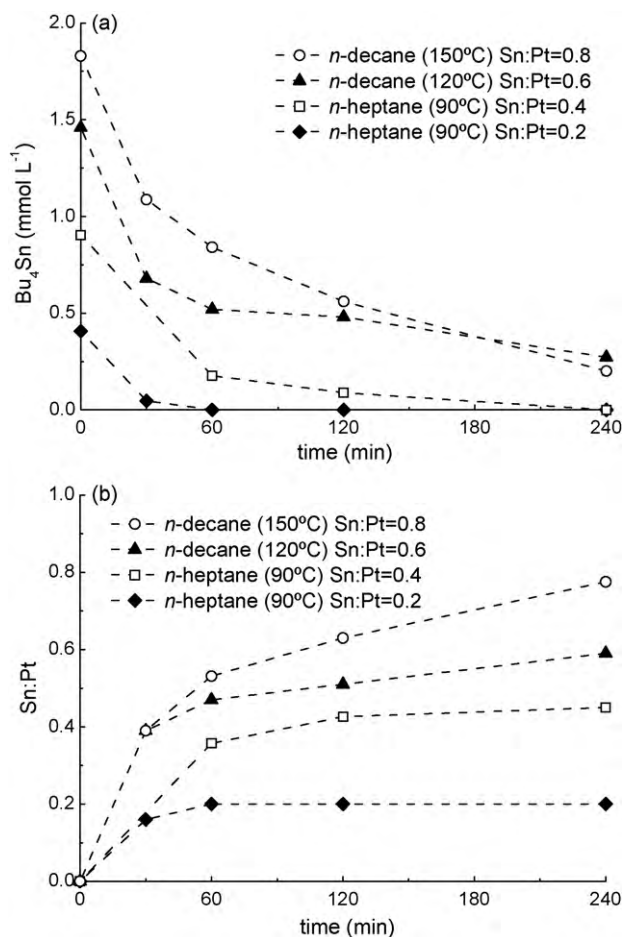
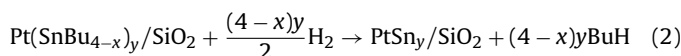
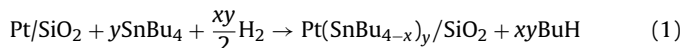


Fig. 2. Variation of the concentration of tetra *n*-butyl tin (SnBu₄) as a function of time for various initial concentrations of the organotin compound.

particles and is homogeneously dispersed through the support surface [23].

Tin-modified catalysts were obtained by a surface controlled reaction between the reduced monometallic catalyst and a SnBu₄ solution, using a paraffinic solvent like *n*-heptane or *n*-decane. This reaction involves a two-step anchoring process: in the first step, the organic groups are anchored to the surface producing an organobimetallic system (temperatures between 90 and 150 °C); the second step corresponds to the formation of the bimetallic phase after the release of all the organic groups (temperatures between 150 and 500 °C). During these steps, the following reactions take place:



Reaction (1) was carried out at two different temperatures: 90 and 120 °C. In Fig. 2a is the variation of concentration of tetra *n*-butyl tin as function of time for various initial concentrations of the organotin compound. Blank experiments carried out on silica support, without metallic platinum, did not yield any detectable reaction of tetra *n*-butyl tin with the support.

In addition to Fig. 1, Table 1 shows the influence of increasing amounts of tin in the platinum particle size (measured by TEM) for the studied materials. The metal particle size distribution was in all cases very narrow, with only slight oscillations in d_{TEM} being observed for the bimetallic systems regarding the original Pt/SiO₂ catalyst. These results are in good agreement with the selective

Table 1

Pt:Sn atomic ratio and Pt particle size (measured by TEM) for SiO₂ supported Pt and PtSn catalysts.

Catalyst	Sn:Pt (atomic ratio)	<i>d</i> _{Pt} (nm)
Pt	–	2.2
PtSn _{0.2}	0.2	2.2
PtSn _{0.4}	0.4	2.2
PtSn _{0.6}	0.6	2.2
PtSn _{0.8}	0.8	2.1

addition of Sn over Pt, already reported with other bimetallic systems prepared by SOMC/M techniques [24–26].

The reaction between SnBu₄ and Pt/SiO₂ was followed by GC analysis, measuring the variation of SnBu₄ concentration in the impregnating solution. The total amount of tetra *n*-butyl tin fixed on the catalysts surface was measured by two different and independent methods: difference between the initial and the final concentration of tetra *n*-butyl tin and by chemical analysis of the samples. A good agreement was found between both methods.

The results reported in Fig. 2b, show that after a certain time of reaction, the amount of tin fixed per superficial Pt (Sn:Pt) reaches a plateau, except for the highest Sn:Pt ratio. Once the reaction is finished, washing the catalyst with *n*-heptane did not remove any significant amount of SnBu₄. Fig. 2b also shows that an increase in the reaction temperature has a beneficial influence on both the SnBu₄ reacted with Pt/SiO₂ and the rate of reaction (1). At 90 °C it was possible to fix tin selectively onto platinum up to a Sn:Pt ratio of approximately 0.40, whereas this quantity increased to 0.8 when the reaction temperature was 150 °C.

The binding energies (BE) of the Pt 4f_{7/2} and Sn 3d_{5/2} levels for Pt/SiO₂, PtSn_{0.2} and PtSn_{0.8} catalysts are reported in Table 2. Additionally, the surface Sn(0)/Pt atomic ratios and the relative amounts of reduced tin (Sn(0)/Sn_{total}), estimated from the integral of the XPS peaks, are also given.

For all the catalysts, the region corresponding to Pt 4f_{7/2} showed a single peak, which is characteristic of platinum in the metallic state [27]. Both bimetallic samples presented a shift of this peak toward lower BE. This fact is indicative of the existence of an electronic effect of tin over platinum, in agreement with previous results obtained in studies performed with PtSn catalysts supported on SiO₂ and Al₂O₃, prepared by SOMC/M techniques [28,29]. The Sn 3d_{5/2} spectra for the bimetallics PtSn = 0.2 and PtSn = 0.8 are plotted in Fig. 3. They present two bands, one centered at ca. 484 eV which can be ascribed to reduced tin [30], and another one at higher BE (486.3 and 487.3 eV for PtSn = 0.2 and PtSn = 0.8, respectively), which is attributed to oxidized tin (Sn(II) and Sn(IV)) [27]. The presence of metallic tin in bimetallic catalysts is an indication for the existence of bimetallic PtSn phases (even alloys), as it has been readily assessed by EXAFS analysis performed on analogous systems as the ones here employed [28].

Although both bimetallic samples have more or less the same Sn(0)/Sn_{total} ratio (Table 2), the Sn(0)/Pt ratio increases when the amount of tin increases, which can be assigned to the following effects: (i) dilution of platinum by metallic tin, due to the formation of SnPt phases and (ii) covering of metal particles surface by oxidized tin species. Taking into account all the XPS results, the catalytic surface maybe depicted by the coexistence of SnPt phases

Table 2

Binding energies (eV) of the Pt 4f_{7/2} and Sn 3d_{5/2} levels for SiO₂ supported Pt and PtSn catalysts.

Catalyst	BE Pt 4f _{7/2} (eV)	BE Sn 3d _{5/2} (eV)	Sn(0):Sn _{total} (atomic ratio)	Sn(0):Pt (atomic ratio)
Pt/SiO ₂	71.6	–	–	–
PtSn _{0.2}	71.1	484.1, 486.3	0.55	0.11
PtSn _{0.8}	70.8	484.2, 487.3	0.59	0.47

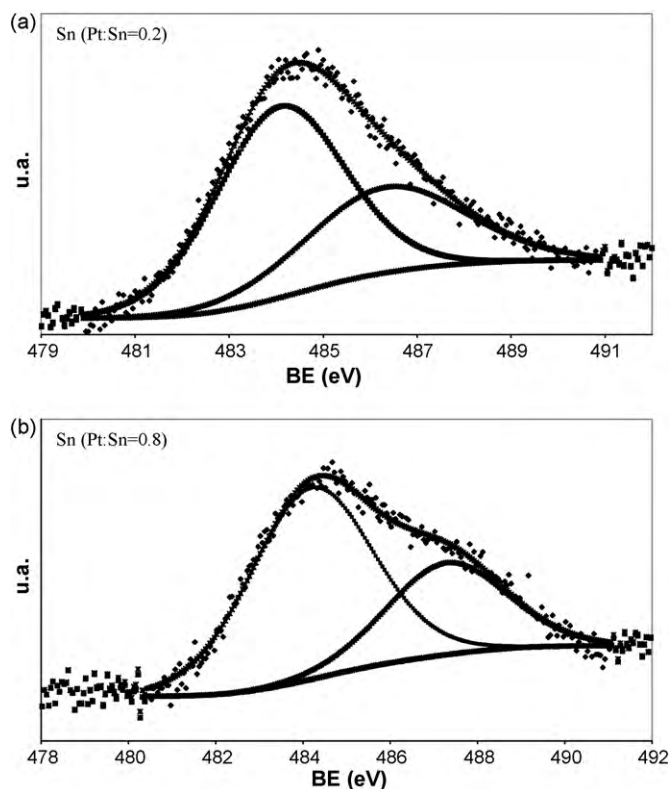


Fig. 3. XPS spectra for the Sn region (Sn 3d_{5/2} level): (a) PtSn = 0.2 and (b) PtSn = 0.8.

(probably alloys), ionic tin located at the platinum–support interface and some segregated metallic platinum.

In order to develop an environmentally friendlier process for Sn addition, it was tested the preparation of bimetallic catalysis in aqueous phase using a water-soluble precursor. Tributyltin hydroxide (Bu₃SnOH) was selected as Sn precursor and was obtained from Bu₃SnCOOCH₃ according to the following reaction:



This reaction was carried out in the presence of KOH (pH = 10) according to a reported procedure [31]. The FT-IR spectrum of the as-synthesized product (Bu₃SnOH) was obtained, and compared to that observed for the precursor (Bu₃SnCOOCH₃). Strong absorption bands at wavenumbers between 2857 and 2957 cm⁻¹ were observed for both compounds, corresponding to C–H stretching modes of butyl groups. For the product, the bands at 1076 cm⁻¹ (assigned to –Sn–O–CO) and 1581 cm⁻¹ (assigned to –O–CO) have almost disappeared, confirming the formation of Bu₃SnOH; the bands in the range 612–409 cm⁻¹ due to Sn–O and Sn–C vibrations, further confirms its formation.

Once synthesized, the Bu₃SnOH was used to prepare bimetallic catalysts with different Sn:Pt ratios (PtSnA and PtSnB) according to SOMC/M methodologies. In this case, the amount of Sn incorporated in the Pt surface was always lower than the nominal value expected.

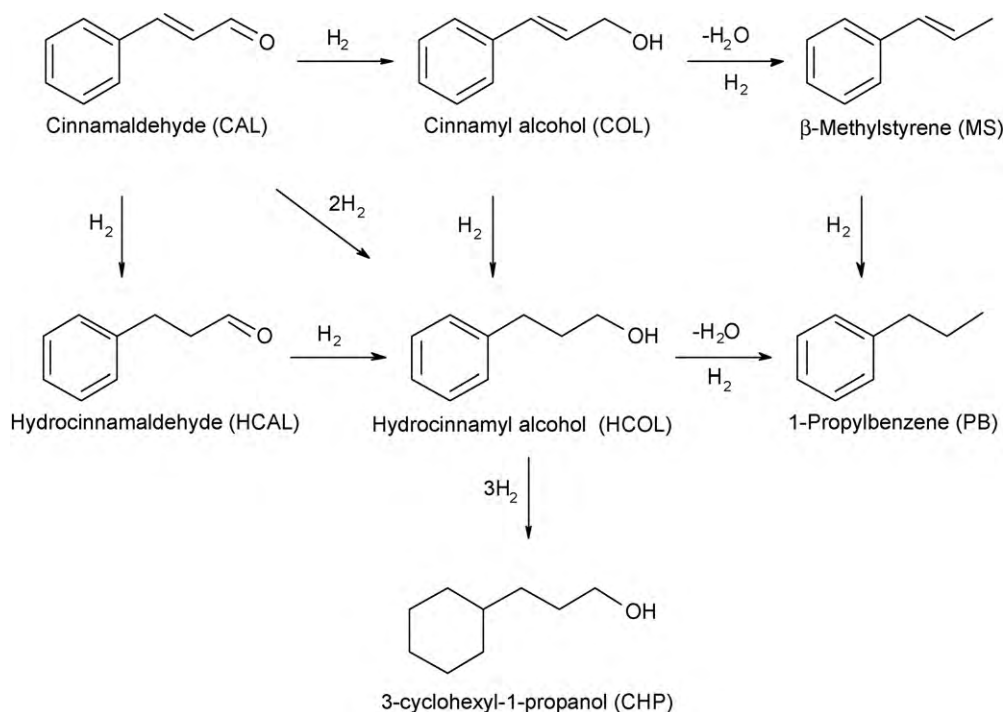


Fig. 4. Reaction scheme proposed for the selective hydrogenation of cinnamaldehyde using SiO₂ supported Pt and PtSn catalysts.

3.2. Selective hydrogenation of cinnamaldehyde

The preferred solvent is *n*-heptane due to high H₂ solubility when compared to other commonly used solvents [8], and because the corresponding acetal and ether cannot be formed during the reaction as opposed to what occurs when alcohol-based solvents are used [6,32].

The reaction pathway proposed for the selective hydrogenation of cinnamaldehyde (CAL) with SiO₂ supported catalysts is shown in Fig. 4. The hydrogenation of CAL involves the parallel and consecutive reduction of different functional groups i.e., C=C and C=O bonds. Typically, a mixture of the desired cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL) and hydrocinnamyl alcohol (HCOL) is obtained. A number of side reactions involving the hydrogenation of aromatic ring (3-cyclohexyl-1-propanol, CHP) and hydrogenolysis can also be detected. In this case, the presence of β -methylstyrene (MS) and 1-propylbenzene (PB) could indicate a strong adsorption of the hydroxyl groups over the metal sites and, thus, a possible poisoning effect [13].

In Table 3 it is presented the turn-over frequency (TOF) results and selectivities to COL, HCAL and HCOL, measured at 60% conversion of cinnamaldehyde, as a function of tin content over the SiO₂ supported catalysts (SnBu₄ was used as Sn precursor for bimetallic catalysts).

Table 3

TOF, initial reaction rate and selectivity results obtained for the hydrogenation of cinnamaldehyde using SiO₂ supported Pt and PtSn catalysts (selectivities measured at 60% conversion).

Catalyst	TOF	r_i^* ($\mu\text{mol s}^{-1} \text{g}_{\text{Pt}}^{\text{superficial}}^{-1}$)	Selectivity (%)			
			COL	HCAL	HCOL	Others ^a
Pt	0.067	106	6	55	8	31
PtSn _{0.2}	0.620	3180	33	30	16	21
PtSn _{0.4}	0.504	2582	42	26	19	13
PtSn _{0.6}	0.146	750	73	9	7	11
PtSn _{0.8}	0.029	147	80	6	4	10

^a PB, MS and CHP.

The Pt/SiO₂ catalyst presents a lower TOF value when compared to the bimetallic ones. In addition, selectivity to the desired cinnamyl alcohol is rather low (<20% throughout the reaction). These selectivity results are similar to those reported for other catalytic systems where metal oxides do not exhibit the SMSI effect after reduction at high temperatures [33,34].

Tin addition to the monometallic catalyst produces a significant change to both product distribution (Fig. 5) and reaction rate (Table 3). With Pt/SiO₂ catalyst, concentration of COL remains very low, whereas that of HCAL is much higher and increases throughout the reaction. After Sn addition there is a total inversion on the preferential pathway between C=C and C=O, regarding the monometallic catalyst. Furthermore, the maximum COL concentration observed is much higher than that observed for HCAL with the Pt catalyst. Selectivity to COL increases as a function of the Sn load, reaching 80% when the catalyst having the highest Sn:Pt ratio is used. Simultaneously, selectivity to HCAL decreased with increasing Sn:Pt ratio.

Selectivity results often depend on the nature of the support where the metal is dispersed. Several examples of how the support can effectively improve selectivity towards the unsaturated alcohol can be found using, for example, zeolites [35–37] or reducible metal oxides [38–40]. In these cases, the enhanced selectivity results are explained in terms of shape selectivity and steric effects due to the presence of small channels and by sub-oxide species decorating the surface of the metal phase, respectively. In the work here presented, the use of SiO₂ discards any promoting effect attributed to the support, being the results entirely ascribed to the nature of the prepared active metal phase.

Besides the improvement in selectivity, tin addition also enhanced the TOF obtained comparing with the monometallic Pt/SiO₂ catalyst. The highest reaction rates and TOF values were obtained using a Sn:Pt ratio of 0.2 and 0.4. This result is in perfect agreement with those previously reported for the hydrogenation of carbonyl compounds using PtSn bimetallic catalysts, and is assigned to the creation of a new type of active site, as a consequence of the specific interaction between SnBu₄ and the supported

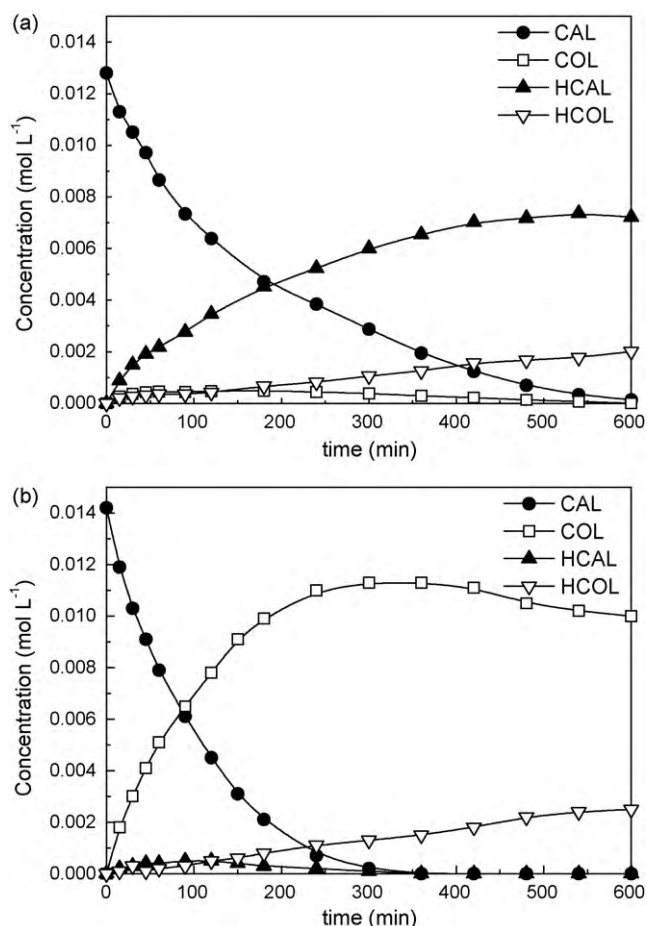
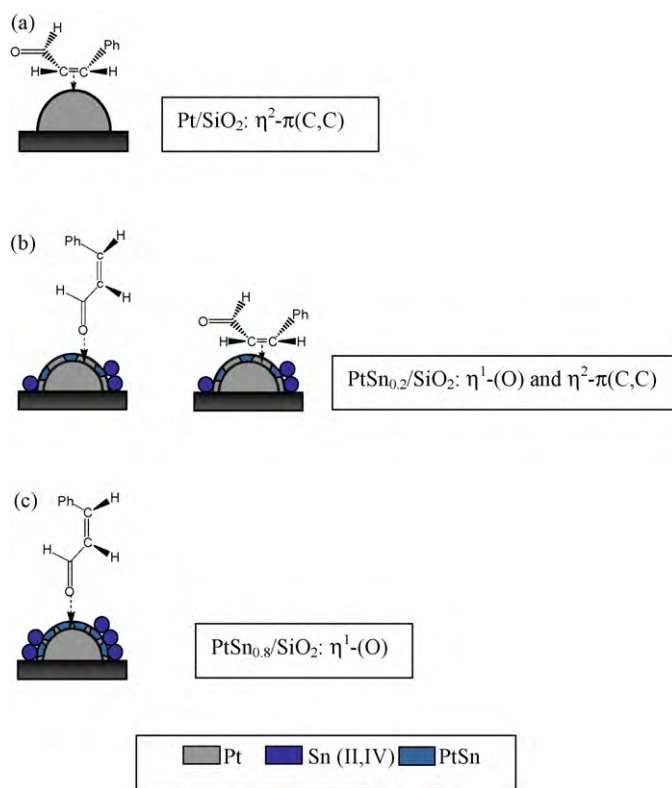


Fig. 5. Product distribution for the selective hydrogenation of cinnamaldehyde using (a) Pt and (b) PtSn_{0.8} catalysts.

and reduced Pt [41]. A higher addition of tin reduces the initial hydrogenation rate and the TOF value, which may be due to the lower number of active sites for the formation of hydrogen atoms. This way, the activity of the bimetallic systems depends on the concentration of tin present in different oxidation status, leading to an optimum in the Sn/Pt atomic ratio.

Catalytic results suggest that cinnamaldehyde hydrogenation on Pt-based supported catalyst occurs through different intermediates depending on the surface properties of the catalyst. Pt/SiO₂ catalyst showed low activity for converting CAL and also a low selectivity towards COL. Delbecq and Sautet have modeled the adsorption of several unsaturated α,β -aldehydes (acrolein, crotonaldehyde, prenal and cinnamaldehyde) using the extended Hückel approach on platinum and palladium crystals [42]. 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. For the case of high dispersions (which is the case of the catalysts here employed), the percentage of Pt (110) and Pt (100) faces is higher and for this reason adsorption of CAL through a η^2 - π (C,C) type would be favored leading to the preferential hydrogenation of the C=C group (Scheme 1a).

The hydrogenation of the C=O group, leading to COL production, shows a noticeable increase in catalysts modified with tin, with respect to the monometallic catalyst. The higher the tin content, the higher the selectivity towards COL. In these catalysts, the dilution of platinum sites would favor the presence of species of the type η^1 -(O) for the adsorption of cinnamaldehyde, inhibiting other forms of chemisorption such as η^2 -(C,C) and η^4 -(C,C,C,O), favorable for the hydrogenation of the C=C group. These geomet-



Scheme 1. Adsorption modes of cinnamaldehyde on Pt and PtSn modified surfaces.

rical modification introduced by tin is more pronounced for the samples with higher tin content, in this way PtSn = 0.8 presents the highest dilution of platinum sites and the highest concentration of species η^1 -(O), correspondingly, the selectivity to COL reaches the highest level (Scheme 1b and c).

Electronic effects must be also important in the chemisorption of the reaction intermediates. The existence of “Lewis acid sites”, due to the presence of ionic tin, tends to promote the H₂ attack to the C=O group and in this way, leads to higher selectivity to COL. This type of electronic modifications seems to play a fundamental role for molecules with phenyl groups, as in the case of the cinnamaldehyde [13].

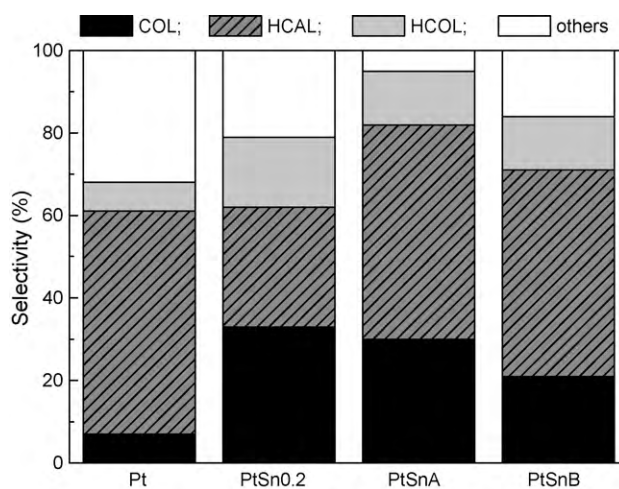


Fig. 6. Effect of the Sn precursor over the selectivity results: Pt (no tin), PtSn = 0.2 (SnBu₄) and PtSnA and PtSnB (nominal amount of tin SnPt = 1.0 and 0.8 respectively) (Bu₃SnOH).

The selective hydrogenation of cinnamaldehyde was also carried out with bimetallic catalysts prepared using a water-soluble Sn precursor (Bu_3SnOH), in order to assess if these materials were as active and selective as those prepared using SnBu_4 . The catalytic results using these materials are depicted in Fig. 6.

Both catalysts provided an enhanced selectivity to COL regarding the Pt/SiO₂ catalyst, as the catalytic behavior was similar to that exhibited by PtSn=0.2 (prepared using SnBu_4). This result is not surprising since the amount of Sn that was successfully introduced using the Bu_3SnOH precursor was rather lower than the nominal load intended, as already indicated in the experimental section. In spite of this, the improvement in selectivity to COL allows us to conclude that SOMC/M techniques can also be performed in the aqueous phase. Thus, this methodology could provide an alternative, environmentally friendlier, pathway to the production of new bimetallic catalysts.

4. Conclusions

Addition of tin to the Pt/SiO₂ monometallic catalyst produced a remarkable shift in both the product distribution and turn-over frequency in the liquid-phase hydrogenation of cinnamaldehyde to cinnamyl alcohol. The selectivity towards cinnamyl alcohol increased with the amount of Sn, reaching 80% with a Sn:Pt ratio of 0.8. The observed reaction rates were also higher after Sn addition, with the highest values being obtained for Sn:Pt ratios between 0.2 and 0.4.

Taking into consideration that Sn does not dissociate H₂, thus, does not possess intrinsic hydrogenation properties, the simultaneous increase of both activity and selectivity indicates the formation of a new type of active site, different in nature when compared with the original Pt.

The selective hydrogenation of cinnamaldehyde was also carried out with PtSn bimetallic catalysts where a water-soluble tin precursor (Bu_3SnOH) was used. Also in this case the catalytic performance was improved regarding the parent Pt/SiO₂ catalyst.

The improvement in selectivity to cinnamyl alcohol allows us to conclude that SOMC/M techniques can also be performed in the aqueous phase, providing an alternative, environmentally friendlier, pathway to the production of new bimetallic catalysts.

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