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ScienceDirect

Catalysis Today 133–135 (2008) 35–41

CATALYSIS TODAY

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Effect of tin content and reduction temperature on the catalytic behaviour of $PtSn/TiO_2$ catalysts in the vapour-phase hydrogenation of crotonaldehyde

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Abstract

This paper reports a study of $PtSn/TiO_2$ catalysts reduced at two different temperatures (473 and 773 K) by infrared spectroscopy of CO adsorbed at 298 K and XPS, as well as their behaviour in the vapour phase selective hydrogenation of crotonaldehyde at 333 K. Catalysts with 2 wt% Pt and different Pt:Sn atomic ratios were prepared by co-impregnation of a commercial TiO_2 (P25, from Degussa) with aqueous solutions of H_2PtCl_6 and $SnCl_2\cdot 2H_2O$. XPS results show that tin is in oxidized state when the catalysts are reduced at 473 K, whereas a proportion is in the metallic state after reduction at 773 K. The amount of surface platinum decreases when the tin loading and the reduction temperature increase. The presence of Pt-Sn alloy in the catalysts after reduction at high temperature has been assessed by *in situ* IR spectroscopy of adsorbed CO, although a proportion of platinum remains in a non-alloyed state. The catalytic activity in the vapour-phase hydrogenation of crotonaldehyde increases after high temperature reduction, and the same behaviour is obtained with selectivity towards the hydrogenation of the carbonyl bond to yield the unsaturated alcohol, the best selectivity being obtained for the catalyst with the lowest Pt/Sn ratio.

Keywords: Pt-Sn catalysts; Titania; Crotonaldehyde hydrogenation; FTIR

1. Introduction

Bimetallic Pt-Sn catalysts, mainly supported on alumina, are widely used in many catalytic processes in petrochemical (reforming, hydrogenation and dehydrogenation of light alkanes) and fine chemical industries (selective hydrogenations), yielding a better performance, in terms of stability and activity, than the monometallic Pt/Al_2O_3 [1,2].

In the field of fine chemicals, the preparation of unsaturated alcohols by the selective hydrogenation of the corresponding α,β-unsaturated aldehydes has a great industrial importance in the synthesis of many products [3,4]. This reaction constitutes a challenging task, since the hydrogenation of the C═C bond is thermodynamically favoured over the hydrogenation of the carbonyl bond, and with traditional hydrogenation catalysts the selectivity towards the unsaturated alcohol is usually low. An improvement in activity and selectivity towards the unsaturated alcohol has been found with the use of bimetallic Pt-Sn catalysts [5]. The promoter effect of tin is attributed to oxidized tin species which, acting as a Lewis acid, interacts with the oxygen atom of the carbonyl bond (basic group), thus weakening the C═O bond and favouring its hydrogenation. However, metallic tin has been also detected by XPS in these systems [6,7]. This metallic tin would be able to form Pt-Sn alloy phases, and the dilution of platinum by tin would destroy the platinum ensembles, lowering the number of sites that strongly interact with hydrogen and chemisorb the α,β-unsaturated aldehyde through the olefinic bond, thus hindering the C═C hydrogenation reaction rate.

Another way to improve the selectivity towards the unsaturated alcohol is the use of a support that can modify the catalytic properties of the dispersed metal or bimetallic system. Tauster et al. [8,9] found that, when partially reducible

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doi:10.1016/j.cattod.2007.11.053

oxides such as TiO_2 are used as support, they can modify the chemisorption behaviour of hydrogen and carbon monoxide on metals from groups 8, 9 and 10 after reduction at high temperature (about 773 K). The term strong metal–support interaction (SMSI) was introduced to label this effect. Vannice found the promoter effect of TiO_2 on metals from group 8 after reduction at 773 K for several reactions [10,11]. A model to explain this behaviour has been proposed, involving the formation of special sites at the interface between the metal and the support. These sites consist of partially reduced TiO_x species (or oxygen vacancies) that coordinate the oxygen atom of the C=O to increase the selectivity towards the hydrogenation of the carbonyl bond [10–12].

In the work presented here, the promoting effect of tin has been studied, in both metallic and oxidized states, in a series of $PtSn/TiO_2$ catalysts with different Pt:Sn atomic ratio, for the selective hydrogenation of crotonaldehyde. The influence of the strong metal–support interaction effect on this reaction is also studied by using low (473 K) and high (773 K) reduction temperature treatments on the catalysts. The catalysts have been characterized, after reduction at both temperatures, by X-ray photoelectron spectroscopy (XPS) and *in situ* infrared spectroscopy of adsorbed CO, this allowing a comprehensive description of the surface composition and the available adsorption sites.

2. Experimental

Degussa P25 (60% anatase, 40% rutile) with a surface area of 50 $m^2\ g^{-1}$ (N_2, 77 K, BET method) was used as a support, which was previously calcined in air at 773 K for 5 h. The $PtSn/TiO_2$ catalysts were prepared by a co-impregnation method, with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (Johnson Matthey) of an appropriate concentration to achieve a Pt content of 2 wt%, and $SnCl_2{\cdot}2H_2O$ (Aldrich). Catalysts with nominal Pt:Sn atomic ratios of 1:2, 2:1, 3:1, and 4:1 were prepared. The slurry was stirred for 12 h and then the excess solvent was removed by heating at 363 K under vacuum in a rotary evaporator. Finally, the catalysts were dried at 383 K for 24 h and calcined in synthetic air at 673 K for 4 h.

XPS spectra were acquired with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg Kα 300 W ($h\nu = 1253.6$ eV, 1 eV = 1.6302×10^{-19} J) 300 W X-ray source. The powder samples were pressed into small Inox cylinders and then mounted on a sample rod placed in a pre-treatment chamber and reduced in H_2 for 1 h at 473 and 773 K before being transferred to the analysis chamber. Before recording the spectra, the sample was maintained in the analysis chamber until a residual pressure of 5×10^{-9} mbar was reached. The spectra were collected at a pass energy of 50 eV. The intensities were estimated by calculating the integral of each peak, after subtraction of the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) lines. Binding energies were referenced to the Ti $2p_{3/2}$ line in TiO_2 at 458.5 eV, which provide values with an accuracy of ±0.2 eV. The surface Pt/Ti and Pt/Sn ratios were estimated from the integrated intensities, after correction for atomic sensitivity factors [13].

In situ IR experiments were carried out using a quartz cell fitted with CaF_2 windows and an external furnace. Catalyst samples were prepared as 16 mm diameter self-supporting disks by pressing 70 mg of loose powder between polished steel dies at 15 MN m^2. Prior to any measurements, samples were reduced *in situ* under a hydrogen flow (50 $cm^3\ min^{-1}$) at 473 or 773 K for 1 h. After reduction, samples were out-gassed at the reduction temperature for 15 min, to a final pressure of $\approx 10^{-5}$ Torr, before cooling to ambient temperature. Pulses of CO were introduced at 298 K using calibrated volumes and an Edward active strain gauge to measure the pressure of the pulse. IR spectra were recorded at 4 cm^{-1} resolution and averaging 25 scans per spectrum.

The vapour-phase hydrogenation of crotonaldehyde (2-butenal) was tested in a micro-reactor at atmospheric pressure and differential conditions. The catalysts (between 0.01 and 0.03 g) were reduced *in situ* at 473 or 773 K under flowing H_2 (50 $cm^3\ min^{-1}$) for 1 h and then cooled under H_2 to the reaction temperature (333 K). The hydrogenation reaction was carried out using a reaction mixture (total flow: 50 $cm^3\ min^{-1}$; H_2/aldehyde ratio of 26) of H_2 and crotonaldehyde (Fluka, >99.5%), which was prepared by passing H_2 through a thermostated saturator (293 K) containing crotonaldehyde. The concentration of reactants and products was determined by online GC with a Carbowax 20 M 58/90 semicapillary column.

3. Results and discussion

3.1. XPS characterization

The binding energies of the Pt $4f_{7/2}$ and Sn $3d_{3/2}$ levels for the catalysts, both freshly prepared (vacuum treatment at room temperature) and reduced *in situ* at 473 and 773 K for 1 h, are reported in Table 1. In some cases two values are given arising from a deconvolution of the main peak into two contributions, with the corresponding contribution to the overall signal in brackets. The surface Pt/Ti atomic ratios are also presented (which can be used as an estimation of the platinum dispersion on the titania support), as well as the surface Pt/Sn atomic ratios. Additionally, the relative amounts of oxidized tin species (Sn_{ox}/Sn_{total}), estimated from the integral of XPS peaks, is also shown.

The Pt 4f spectra for the unreduced and reduced catalysts are compared in Fig. 1. For all catalysts, the spectra can be deconvoluted into two peaks, the one at lower binding energy corresponding to Pt $4f_{7/2}$ level and the second one, at higher binding energies, to the Pt $4f_{5/2}$ level. For all catalysts, the peaks are quite similar, and for the shake of brevity, only the Pt 4f spectra for the catalyst with atomic ratio Pt:Sn = 1:2 is discussed and shown. For the unreduced catalyst, the peak corresponding to the Pt $4f_{7/2}$ level is centered at 72.5 eV, and it is assigned to oxidized platinum species. The exact assignation of this peak is not easy, because the binding energy of core electrons is not only affected by the metal oxidation state but also by the ligand atoms to which they are coordinated. The

Table 1
XPS characterization of $PtSn/TiO_2$ catalysts

Catalyst	Treatment	Pt $4f_{7/2}$ B.E. (eV)	Sn $3d_{5/2}$ B.E. (eV)	Pt/Ti	Pt/Sn	Sn_{ox}/Sn_{total}
$PtSn/TiO_2$ (4:1)	Unreduced	72.7	487.0	0.0308	1.137	1
	Red. 473 K	71.1	486.2	0.0312	1.063	1
	Red. 773 K	70.5	485.2–487.4	0.0140	0.509	0.54
$PtSn/TiO_2$ (3:1)	Unreduced	72.5	486.7	0.0269	0.724	1
	Red. 473 K	71.4	486.5	0.0253	0.781	1
	Red. 773 K	70.8	484.9–486.9	0.0177	0.410	0.56
$PtSn/TiO_2$ (2:1)	Unreduced	72.6	486.8	0.0219	0.492	1
	Red. 473 K	71.2	485.9	0.0264	0.687	1
	Red. 773 K	71.2	485.0–486.8	0.0184	0.468	0.61
$PtSn/TiO_2$ (1:2)	Unreduced	72.5	486.5	0.0243	0.210	1
	Red. 473 K	71.4	486.5	0.0226	0.225	1
	Red. 773 K	71.1	484.8–486.6	0.0148	0.151	0.86

binding energy of the Pt $4f_{7/2}$ level for Pt(IV) coordinated to six chlorine atoms (as in the platinum precursor used for the preparation of the catalysts) is reported to be about 75.3 eV (for K_2PtCl_6), but it increases to 74.8 eV for PtO_2 and further to 74.2 eV for $Pt(OH)_4$. Additionally, the binding energies of the Pt 4 $f_{7/2}$ level for $PtCl_2$ is reported to be about 73.4 eV, whereas that for $Pt(OH)_2$ is about 72.4 eV [13]. Therefore, the XPS of the unreduced catalyst would suggest that a certain level of dechlorination of the platinum precursor has taken place. After the reduction treatments (at 473 and 773 K), a single peak appears for the level, which is centered at 71.4 and 71.1 eV for the catalyst reduced at 473 and 773 K, respectively. These binding energies are characteristic of platinum in metallic state. The binding energy is lower when the sample is reduced at 773 K, and this can be attributed to several factors, such as a decrease in the chloride levels on the surface or even metal sintering.

The Sn $3d_{5/2}$ spectra for the unreduced and reduced catalysts are plotted in Fig. 2. The spectra indicate a shift of the binding energy towards lower values with increasing reduction

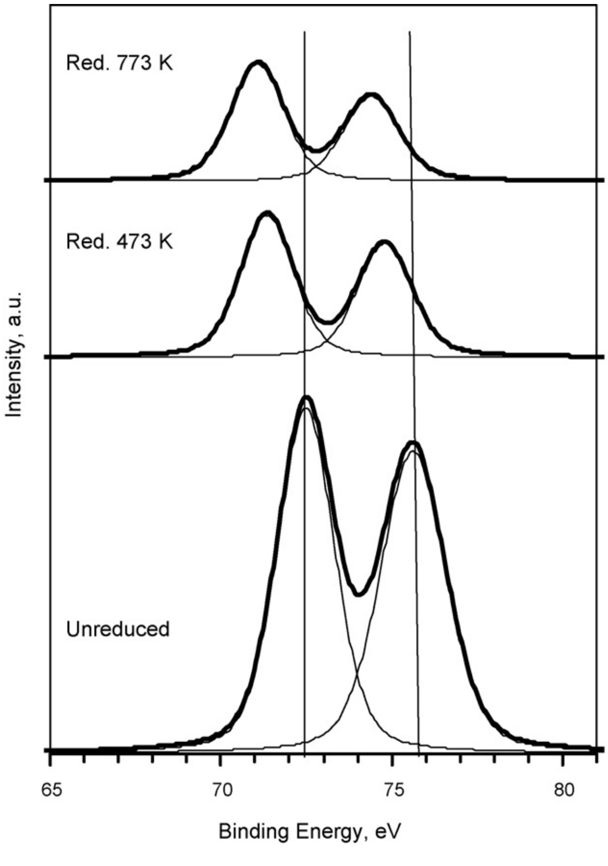

Fig. 1. XPS Pt 4f spectra of the unreduced and reduced $PtSn/TiO_2$ catalysts with atomic ratio Pt:Sn = 1:2.

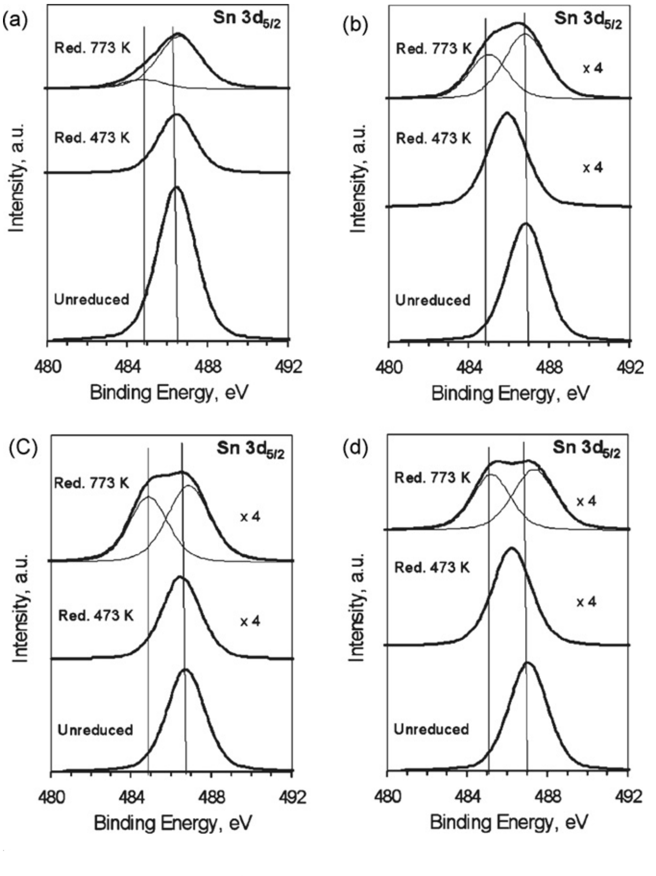

Fig. 2. XPS Sn 3d spectra of the unreduced and reduced $PtSn/TiO_2$ catalysts with atomic ratio Pt:Sn (a) 1:2, (b) 2:1, (c) 3:1 and (d) 4:1.

temperature, thus indicating the reduction of oxidized tin species. For the unreduced catalyst and the one reduced at 473 K, only one band is observed which is centered between 486.2 and 487 eV, and it is assigned to oxidized tin species. After reduction at 773 K, a second band appeared at lower binding energy (around 485 eV), which is characteristic of metallic tin. Therefore, the surface composition of the bimetallic catalysts reduced at 473 and at 773 K is different. Whereas platinum is in metallic state after both reduction treatments, tin is in oxidized state when catalysts are reduced at 473 K, and in both oxidized and metallic states after reduction at 773 K. The presence of metallic tin in the catalysts reduced at 773 K opens up the possibility for the existence of Pt-Sn alloy phases after this treatment, although this cannot be readily assessed by XPS.

Discrimination between Sn(II) and Sn(IV) species with XPS is difficult. Therefore, the aim of the deconvolution procedure was to separate the contributions of oxidized and metallic tin species. The ratio between the amount of oxidized tin species and the total amount of tin (Sn_{ox}/Sn_{total}) depends on the Pt:Sn ratio. Table 1 shows that the relative amount of Sn_{ox} decreases when the Pt:Sn ratio increases. That is it decreases when the total amount of tin decreases.

When the catalysts are reduced at 473 K, the Pt/Ti atomic ratio decreases as the amount of tin increases. This would be consistent with coverage of the platinum particles by oxidized tin species. The same effect is observed after the reduction treatment at 773 K. In the latter case, this might arise due to: (i) dilution of the platinum by metallic tin, upon the formation of Pt:Sn bimetallic phases, and (ii) formation of partially reduced titanium oxide, TiO_{2-x}, that can migrate onto the surface of the metallic particles leading to partial decoration.

Finally, the Pt/Sn atomic ratio decreases when the amount of tin loading increases, and when the catalysts are reduced at 773 K, which can be also attributed to the effects previously discussed. This drop in the Pt/Sn atomic ratio is lower when the amount of tin loaded increases. On the other hand, the Pt:Sn surface atomic ratio is always lower than in the bulk, which indicates a significant surface enrichment with tin species.

3.2. *Infrared spectroscopy*

Fig. 3 shows the FTIR spectra of CO adsorbed on different $PtSn/TiO_2$ catalysts after reduction at 473 K. For the shake of clarity, only spectra for catalysts with atomic ratio Pt:Sn = 4:1, 2:1 and 1:2 have been plotted. In all cases, catalysts reduced at 473 K have been exposed, at 298 K, to increasing CO doses until reaching 50 Torr, followed by evacuation in high vacuum for 1 h at 298 K. All spectra exhibit bands in the 2150–2000 cm^{-1} region, that are assigned to CO linearly adsorbed on the different metallic sites. The IR spectrum obtained after introduction of a CO dose of less than 0.1 Torr contains only a broad band centered at 2072 cm^{-1}, as well as a low frequency shoulder at 2040 cm^{-1}. An increase in the CO pressure produced a blue shift (2080–2084 cm^{-1}), as well as an increase in the intensity of the bands. The bands are now composed of two or more contributions, with the relative intensity of the highest frequency component being enhanced to a greater extent by an increase in the CO pressure. A band of low intensity at 1890 cm^{-1} is also observed, which corresponds to bridge-bonded CO. A further band at 2188 cm^{-1} assigned to CO adsorbed on the support [14], disappeared after evacuation at 298 K.

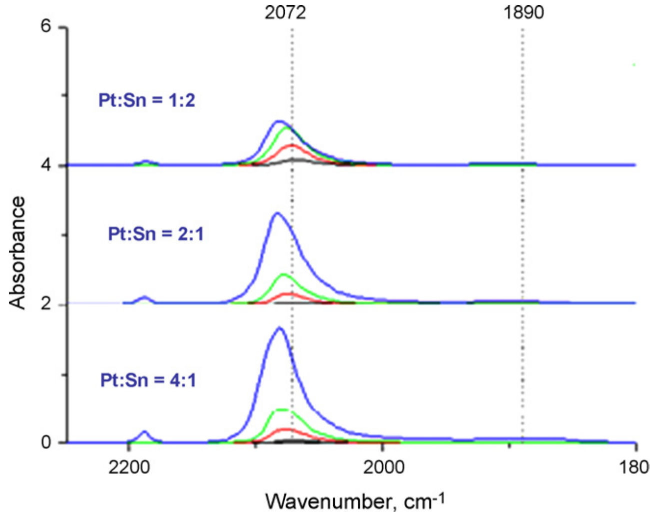

Fig. 3. Infrared spectra of $PtSn/TiO_2$ catalysts with different Pt:Sn atomic ratio reduced at 473 K and exposed to <0.1 (▬), 0.1 (▬), 0.2 (▬) and 50 (▬) Torr CO at 298 K.

The shape of the peaks is similar in all the spectra, but the intensity in the spectral region for CO linearly adsorbed, decreases with the Pt:Sn atomic ratio. This can be explained by a loss of surface platinum when the amount of tin loaded increases, consistent with XPS results.

When the catalysts are reduced at 773 K (Fig. 4), the bands corresponding to linearly adsorbed CO are detected at lower wavenumbers. In this case, a maximum in intensity at 2062 cm^{-1} appears at low coverage and, as in the previous spectra, it is followed by a shoulder at 2040 cm^{-1}. The maximum is blue-shifted (around 2070–2080 cm^{-1}) at high CO coverage.

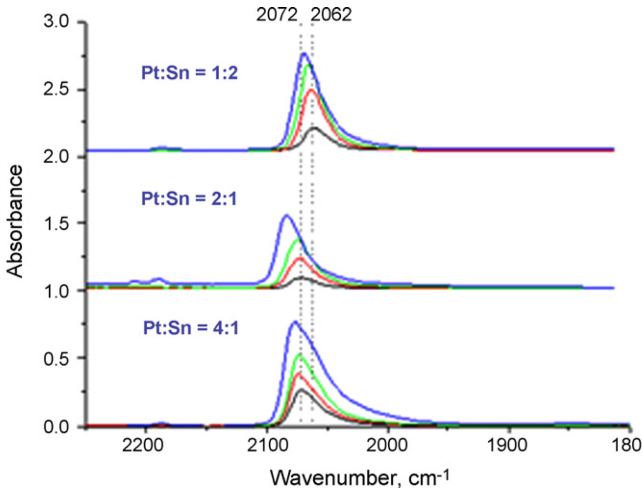

Fig. 4. Infrared spectra of $PtSn/TiO_2$ catalysts with different Pt:Sn atomic ratio reduced at 773 K and exposed to <0.1 (▬), 0.1 (▬), 0.2 (▬) and 50 (▬) Torr CO at 298 K.

In the region of bridging carbonyls, there is only one small band (at 1850 cm^{-1}) at high coverage in the catalyst with Pt:Sn atomic ratio of 4:1. There are also two bands that appear at high coverage, at 2188 and 2207 cm^{-1}, which correspond to CO adsorbed in non-reduced and partially reduced titania, respectively. These bands disappear after evacuation under vacuum at 298 K.

From a comparison of these results with those obtained with the monometallic catalyst, Pt/TiO_2 [15], it can be concluded that the band corresponding to linearly adsorbed CO is present at lower wavenumbers in the presence of Sn. Previous IR studies of CO adsorption on PtSn catalysts, have attributed this to geometric [16,17], electronic [18–20], or a sum of both effects. In this work, results can be explained simply by a geometric effect, although electronic effects cannot be ruled out, given that the addition of tin could make Pt either electron deficient *via* interaction with Sn(II) ions, obtaining a shift to higher wavenumbers, or electron rich *via* formation of a solid solution of Sn in Pt, yielding in this case a negative (red) shift [18].

There is no displacement of the main IR bands to higher wavenumbers in the CO spectra of catalysts reduced at 473 K. Bands can be assigned from single crystal studies, considering coordination numbers and the number of neighbouring sites likely to result in coupling interactions [21–23]. The predominant band can be attributed to CO linearly adsorbed on terrace sites with limited extension or where the metal atoms are present in more open arrangements such as in (1 0 0) facets. Low frequency components also arise due to the deposition of tin oxide on the surface of the particles of platinum. This would reduce the number of dipolar coupling interactions experienced by each Pt-carbonyl, reducing the extent to which band intensity is transferred from low to high to wavenumber components. The band at 1890 cm^{-1} is associated to CO adsorbed in a two-fold-bridging mode on the close packed terrace sites [24,25]. There is a loss of intensity when compared with previous studies on monometallic Pt/TiO_2 [15] catalysts, which is consistent with the idea of tin oxide on the surface of platinum, due to changes in the local site geometry of the remaining exposed adsorption sites.

Reduction at 773 K produces a drastic decrease in IR band intensity, indicating a low CO uptake which correlates with the atomic Pt/Ti ratio obtained by XPS. This is not due to sintering of platinum particles, as larger particles would yield a higher proportion of CO adsorbed on close packed terrace sites such as (1 1 1) patches, resulting in a band at higher frequency. This loss in adsorption capacity can be associated with the migration of partially reduced titania particles to the platinum surface (SMSI effect) [14].

On the other hand, the band of CO linearly adsorbed does not shift to higher wavenumbers when the coverage is increased. This is consistent with expectations for a geometric effect due to the formation of Pt-Sn alloy. The presence of metallic Sn would dilute the concentration of surface Pt atoms and, therefore, would reduce the number of dipolar coupling interactions experienced by each Pt-carbonyl [16,26]. Although a blue shift in the band position is observed at high coverage, it reflects that not all the surface platinum is present in the Pt-Sn alloy phase(s). On comparing with the catalyst reduced at 473 K, there is a red shift of the band position, which is explained by the existence of a close interaction between Pt and Sn leading to an enhanced electron density on Pt [18,20,27].

Finally, the band corresponding to bridge-bonded CO was practically absent in all the catalysts reduced at 773 K. This can be explained by two effects: (i) the migration of partially reduced titania species to the surface of the metallic particles and (ii) the formation of Pt-Sn alloy.

3.3. Crotonaldehyde hydrogenation

Fig. 5a shows the evolution of catalytic activity (µmoles of crotonaldehyde transformed per second per gram of platinum) as a function of time on stream at 333 K for the catalysts reduced at 473 K. The initial data were taken when the carbon balance was achieved. Prior to this, reactant and products were adsorbed by the catalysts and no reliable data could be obtained.

After an initial period of deactivation in the first 50 min of reaction, the activity in all the catalysts remained practically stable with time on stream. The catalyst with an atomic ratio Pt:Sn = 3:1 has the highest activity (500 µmol s^{-1} g Pt^{-1}), followed by the 4:1, 2:1 and 1:2 (435, 105 and 20 µmol s^{-1} g Pt^{-1}, respectively). This suggests that tin has

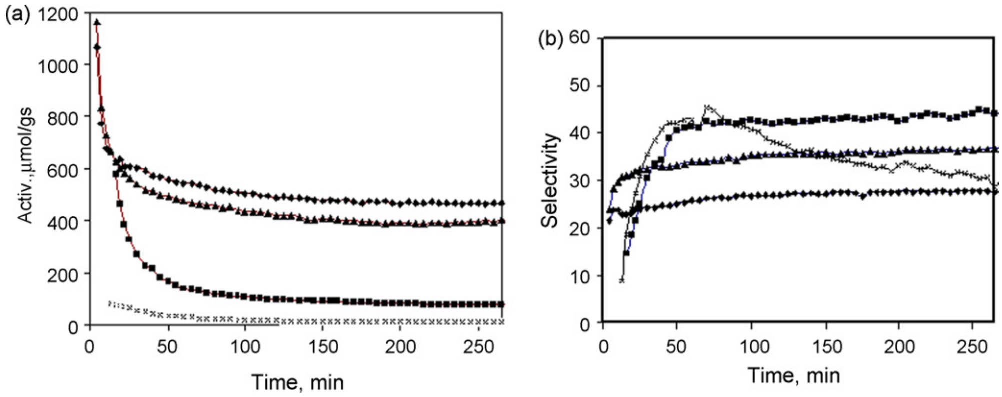

Fig. 5. Evolution of (a) activity and (b) selectivity towards crotyl alcohol for crotonaldehyde hydrogenation with time on stream at 333 K for $PtSn/TiO_2$ catalysts with atomic ratio Pt:Sn 4:1 (▲), 3:1 (◆), 2:1 (■) and 1:2 (×) reduced at 473 K.

a promoting effect in the activity until reaching an optimum content and, after that, higher amounts of Sn has a detrimental effect.

When the catalysts are reduced at 773 K, the trend of the activity with the time on stream is quite similar (Fig. 7a), with a high activity during the first stages of the reaction, catalyst deactivation and a nearly stable activity after about 150 min on stream. It can be clearly seen that the catalytic activity is higher after reduction at high temperature (773 K). For a monometallic Pt/TiO_2, the opposite behaviour was found [15].

Taking into account XPS and FTIR results, there is a loss of platinum atoms in the catalyst surface when the catalysts are reduced at high temperature. This can be assigned to the induction of the SMSI effect, which is characterized by the decoration of the metal particles by patches of partially reduced titania species, and also a diluting effect due to the formation of Pt-Sn alloy phases. It can be asserted that the remaining platinum atoms are much more active thanks to the interfacial sites created after the reduction step at high temperature and due to alloy formation.

In the hydrogenation of crotonaldehyde, a molecule containing two conjugated double bonds, two primary hydrogenation routes can take place (Fig. 6): (i) the hydrogenation of the olefinic C=C bond to yield butanal and (ii) the hydrogenation of the C=O bond to yield crotyl alcohol. These compounds can be further hydrogenated to produce butanol and butane, and crotyl alcohol can also isomerise to butanal. Moreover, decarbonylation could also take place, yielding light hydrocarbons (C_{1-3}). The extend of the secondary reactions depends on the total conversion; therefore, the selectivity towards crotyl alcohol usually decreases when the conversion increases [6,7,28].

In this study, the only reaction products detected were butanal, crotyl alcohol and a small amount of butane and butanol. Fig. 5b compares the selectivity towards crotyl alcohol as a function of time on stream for the PtSn/TiO_2 catalysts reduced at 473 K. The tendency is quite similar for the catalysts with Pt:Sn atomic ratio of 4:1, 3:1 and 2:1. There is an increase in selectivity during the first minutes of reaction, reaching a nearly constant value. The highest selectivity (44%) is achieved by the catalyst with the atomic ratio Pt:Sn = 2:1, followed by 4:1 and 3:1 (36 and 28%, respectively). Comparing these results with previous studies on Pt/TiO_2 monometallic catalysts [15], it can be concluded that the addition of tin stabilize the selectivity towards crotyl alcohol, although there is no direct relationship between the selectivity and the amount of tin loading.

On the other hand, the selectivity towards crotyl alcohol for the catalyst with an atomic ratio Pt:Sn = 1:2 increases quickly in the first minutes on stream, reaching a maximum of 45%, and then decreases until reaching a value of 25% at the end of the reaction (time on stream = 300 min). In this case, the addition of high levels of tin has a negative effect on the selectivity. Furthermore, it decreases with the time on stream after first 100 min.

The evolution of the selectivity towards crotyl alcohol as a function of time on stream when the catalysts are reduced at high temperature (773 K) is quite similar (Fig. 7b). It remains practically constant with time on stream. For all catalysts, the selectivity towards crotyl alcohol was increased as compared to that obtained with catalysts reduced at low temperature (473 K), except for the catalyst with atomic ratio Pt:Sn = 1:2, for which the selectivity practically does not change. The increase in selectivity towards crotyl alcohol with the reduction temperature can be explained as the sum of two effects. On one hand, the decoration of the metal particles by partially reduced titania, with the formation of new sites at the metal–partially reduced titania support interface that can activate the carbonyl bond favouring its hydrogenation. On the other hand, the number of sites which are able to hydrogenate the C=C bond decreases with tin addition due to a dilution of platinum by tin in the Pt-Sn alloy phases formed. Therefore, the amount of sites that strongly interact with hydrogen and chemisorb crotonaldehyde through the olefinic bond would decrease, this reducing the C=C bond hydrogenation reaction rate [7].

When the catalysts are reduced at 773 K there is an inverse relationship between catalytic activity and selectivity towards

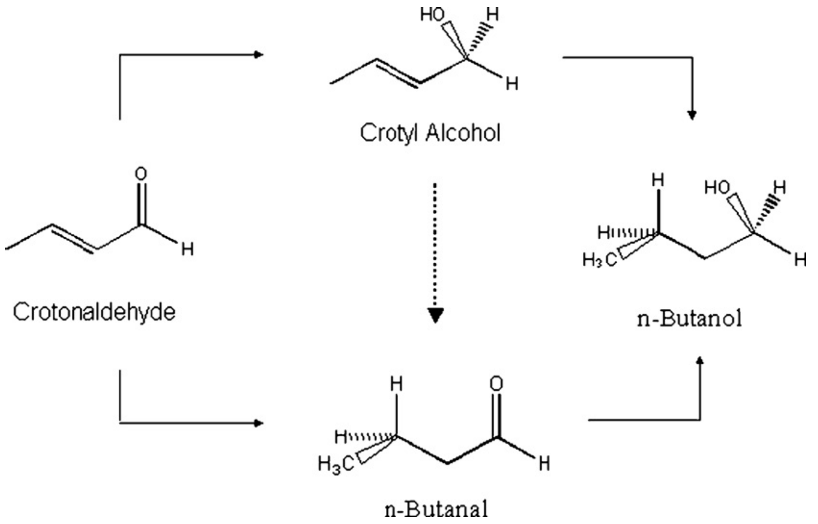

Fig. 6. Diagram of principal products in the hydrogenation of crotonaldehyde.

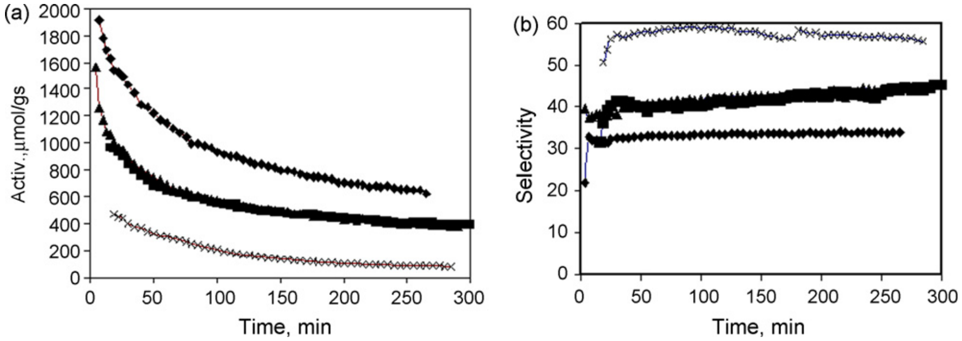

Fig. 7. Evolution of (a) activity and (b) selectivity towards crotyl alcohol for crotonaldehyde hydrogenation with time on stream at 333 K for PtSn/TiO$_2$ catalysts with atomic ratio Pt:Sn 4:1 (▲), 3:1 (◆), 2:1 (■) and 1:2 (×) reduced at 473 K.

crotyl alcohol. The sample with the lowest selectivity ($\approx$34%) has the highest activity and a low tin content (Pt:Sn = 3:1), whereas the sample with the highest selectivity ($\approx$60%) has the lowest activity and the highest tin content (Pt:Sn = 1:2). Taking into account previous studies with a Pt/TiO$_2$ monometallic catalyst [15], bimetallic catalysts have a higher activity and selectivity towards crotyl alcohol, this proving the important role of the tin is this system. The formation of Pt-Sn alloy phases to a greater extent in the catalysts with the highest amount of tin could explain the high selectivity obtained, this correlating with a decrease in the activity due to the dilution of the platinum surface atoms by the formation of Pt-Sn alloy. The possibility of an interaction between the support and different tin species that could affect the platinum performance could be also taken into account.

The overall conversion in all cases was kept into a range from 2 to 10%. Nevertheless, there are no important changes in the selectivity towards crotyl alcohol with conversion.

4. Conclusions

In this work, the catalytic behaviour of bimetallic PtSn/TiO$_2$ catalysts with different Pt:Sn atomic ratio is compared, after reduction at low (473 K) and high (773 K) temperature, for the vapour phase selective hydrogenation of crotonaldehyde. XPS results show that tin is in oxidized state when the samples are unreduced and reduced *in situ* at 473 K, whereas at high reduction temperature, a given amount of tin is in metallic state. The amount of surface platinum decreases when the samples are reduced at high temperature and when the amount of tin loaded increases, by *in situ* IR spectroscopy the presence of Pt-Sn alloy after reduction at high temperature is assessed, although platinum without forming Pt-Sn alloy is still remaining on the surface. The effect of reduction at high temperature is a dramatic increase in catalytic activity for crotonaldehyde hydrogenation, and, in most cases, an increase in the selectivity towards crotyl alcohol. Catalyst with the highest amount on tin (Pt:Sn = 1:2 atomic ratio) reduced at 773 K has shown the best performance in the selectivity towards crotyl alcohol. The combined effects of the decoration of metallic particles by partially reduced titania and PtSn alloy formation are suggested as being the main factors of this behaviour.

Acknowledgments

The authors thank the financial support by the Ministerio de Educación y Ciencia, Spain (Project BQU2003.06150). J.R.-M. also thanks M.E.C. (Spain) for his FPI grant, and for a travel grant to the University of Aberdeen. Thanks to Dr. R.P.K. Wells (University of Aberdeen) for facilitating the latter and for helpful discussions.

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