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Influence of the preparation method on the catalytic behaviour of PtSn/TiO_2 catalysts

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Abstract

PtSn/TiO_2 catalysts containing 2 wt% Pt and a Pt:Sn atomic ratio of 2:1 and 1:1 were prepared by coimpregnation or successive impregnation method with aqueous solutions of $SnCl_2{\cdot}2H_2O$ and $H_2PtCl_6{\cdot}6H_2O$ of a commercial TiO_2 (P25, from Degussa). Both catalyst series, independent of the preparation method, were reduced at 473 and 773 K. XPS results show that tin was in an oxidized state after reduction at 473 K, and that a fraction was in the metallic state after reduction at 773 K. By use of *in situ* FTIR spectroscopy of adsorbed CO, the presence of bimetallic Pt–Sn phases was assessed after reduction at 773 K. Microcalorimetric analysis of CO adsorption enthalpy indicates that reduction at 773 K causes the appearance of a more heterogeneous distribution of active sites, as well as a loss in the amount of sites. The catalytic activity for the gas phase hydrogenation of crotonaldehyde was greatly improved when the catalysts were prepared by coimpregnation, at both reduction temperatures. The selectivity toward crotyl alcohol was higher after reduction at 773 K and independent of the preparation method, although it increased with the amount of tin, suggesting a promoting effect of tin on this reaction.

Keywords: Pt–Sn catalysts; Preparation method; Crotonaldehyde hydrogenation; FTIR

1. Introduction

Supported bimetallic PtSn catalysts are widely used for reforming and dehydrogenation of hydrocarbons in the petroleum industry and for selective hydrogenation reactions in fine chemistry because of their better performance, in terms of activity and stability, than monometallic platinum catalyst [1–5]. As an example, the addition of tin to platinum modifies the selectivity in naphtha reforming, resulting in a higher resistance against deactivation by coke deposition [5].

In the field of fine chemistry, the selective hydrogenation of α,β-unsaturated aldehydes to obtain the corresponding unsaturated alcohols is a reaction of industrial importance. In addition, it is a suitable model reaction to investigate the effect of the catalyst structure on the selectivity. Since the hydrogenation of the C=C bond is thermodynamically favoured, the selectivity toward the unsaturated alcohol is generally poor. In this case, monometallic platinum catalysts give no or a very low selectivity toward the unsaturated alcohol. An improvement in the selectivity can be often obtained by the addition of a second metal of the first transition row, a p block metal or an alkali element. Previous studies reported the use of Fe [6], Ga, Ge, Sn [7–14] and K [15,16]. The enhancement of catalytic selectivity by addition of tin has been explained as a result of the cooperation of two phenomena. On one hand, the carbonyl group is activated by ionic tin species, which interact with the oxygen atom of the carbonyl bond and thus facilitate its hydrogenation. On the other hand, the dilution of platinum atoms by metallic tin hinders the hydrogenation of the C=C bond and suppresses the readsorption of the unsaturated alcohol formed, thus inhibiting its isomerisation to the saturated aldehyde and even its further hydrogenation to the saturated alcohol [12,14,17,18].

Another way of improving the selectivity toward the unsaturated alcohol is the use of supports such as CeO_2 [19–21], TiO_2 [11,22], ZnO [23], MgO [18], or SnO_2 [24] that can modify the catalytic properties of the dispersed metal or bimetallic system. Tauster et al. [25,26] found that the use as a support of a partially reducible oxide, such as TiO_2, could modify the chemisorption ability of metals from groups 8, 9 and

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10 for hydrogen and carbon monoxide after reduction at high temperature (about 773 K). The term "strong metal–support interaction (SMSI)" was introduced to describe this effect. Furthermore, it was demonstrated that this interaction could also modify the activity and selectivity of noble metal in different reactions, such as those involving molecules containing carbonyl bonds. Vannice et al. found the promoter effect of TiO_2 on metals from group 8 after reduction at 773 K for several reactions. They showed that the activity for CO hydrogenation was much greater on Pd/TiO_2 in the SMSI state than for palladium supported on silica, alumina, or silica–alumina [27,28]. Similar results have been found during hydrogenation of acetone [29], crotonaldehyde [22,30,31], acetophenone [32], phenylacetaldehyde [33], and benzaldehyde [34] on Pt/TiO_2 catalysts. Resasco and Haller [35] proposed a model involving a delocalized charge transfer from the metal to TiO_2 after low temperature reduction, and a localized charge transfer from the support to the metal after high temperature reduction. Some years later, these authors suggested that the migration of reduced species from the support onto the metal particle occurred after reduction at high temperature [36]. This geometrical effect would account for the decrease in the chemisorption capacity of hydrogen and carbon monoxide of the catalysts in the SMSI state, because the amount of surface platinum atoms is diminished. Moreover, the creation of special sites at the interface between the metal and the partially reduced support would account for the enhanced selectivity toward unsaturated alcohols. These sites, which consist of partially reduced TiO_x species (Ti^{3+} or oxygen vacancies) would interact with the oxygen atom of the carbonyl group, weakening the bond and thereby facilitating hydrogenation.

The preparation mode of bimetallic catalysts has a great importance, because the interaction between both metals and the support, which determines the catalytic behaviour, depends greatly on the preparation method used. The aim of this work has been the study of bimetallic $PtSn/TiO_2$ catalysts, with different Pt:Sn atomic ratios prepared by two different methods: coimpregnation of both metal precursors or successive impregnation with the tin precursor loaded first. The catalysts were tested in 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.

2. Experimental

Degussa P25 TiO_2 (60% anatase, 40% rutile), with a surface area of 50 $m^2\ g^{-1}$ (N_2, 77 K, BET method) was used as support, which was previously calcined in air at 773 K for 5 h. Two $PtSn/TiO_2$ catalysts were prepared by a coimpregnation method (C-$PtSn/TiO_2$), with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (Johnson Matthey) of the 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 1:1 and 2:1 were prepared. The slurry (10 ml/g of support) 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 under a flow of synthetic air at 673 K for 4 h, with a heating rate of 5 °C/min.

Two more $PtSn/TiO_2$ catalysts, with the same composition as samples prepared by coimpregnation, were prepared by a successive impregnation method (S-$PtSn/TiO_2$). The support was first impregnated with an aqueous solution of $SnCl_2{\cdot}2H_2O$ (Aldrich) and dried at 383 K overnight, and then it was impregnated with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (Johnson Matthey). Drying and calcination treatments were the same as described for the coimpregnated catalysts.

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 of 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 [37].

FTIR 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. FTIR spectra were recorded after each pulse without outgassing at 4 cm^{-1} resolution and averaging 25 scans per spectrum.

Microcalorimetric measurements were performed at 298 K using a Setaram BT2.15D heat-flux calorimeter. The calorimeter was connected to a volumetric system employing a Baratron capacitance manometer for precision pressure measurement (±0.001 Torr). The maximum leak rate of the volumetric system (including the calorimetric cell) was 10^{-5} Torr min^{-1} min in a system volume of approximately 60 cm^3. The samples (between 0.3 and 0.8 g) were reduced *ex situ* in high purity hydrogen (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, and then purged at the same temperature for 1 h in high purity helium to remove any adsorbed hydrogen. The samples were sealed in a Pyrex NMR tube and placed in a special calorimetric cell. When thermal equilibrium was reached, the capsule was broken, and small pulses of CO were introduced until the catalyst became saturated. The resulting heat response for each pulse was recorded as a function of time and integrated to determine the energy released. The differential heat (kJ mol^{-1}) was defined as the negative of the enthalpy change of adsorption per mole of gas adsorbed.

The vapour-phase hydrogenation of crotonaldehyde (2-butenal) was carried out in a micro-reactor at atmospheric pressure operating under 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 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 thermo-stabilised 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 reduced *in situ* at 473 and 773 K for 1 h are reported in Table 1. In some cases two values are given, as a result of the deconvolution of the main peak into two contributions. 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, are also given.

The Pt 4f spectra for the S-PtSn/TiO_2 (2:1) catalyst reduced at 473 and 773 K are compared in Fig. 1. In this region, the spectra show two peaks. The one at lower binding energy corresponds 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 sake of brevity, only the Pt 4f spectra for the catalyst S-PtSn/TiO_2 (2:1) is shown and discussed. When the sample was reduced at 473 K a single peak, centred at 71.2 eV, appears for the Pt $4f_{7/2}$ level. This value is characteristic of platinum in the metallic state. After reduction at 773 K the peak is shifted to lower binding energy, 70.6 eV, and this can be attributed to several factors, such as a decrease in the surface chloride levels or even metal sintering. It should be noted that the intensity of the peak is lower when the sample is reduced at higher temperature, indicative of a lower amount of detectable surface platinum.

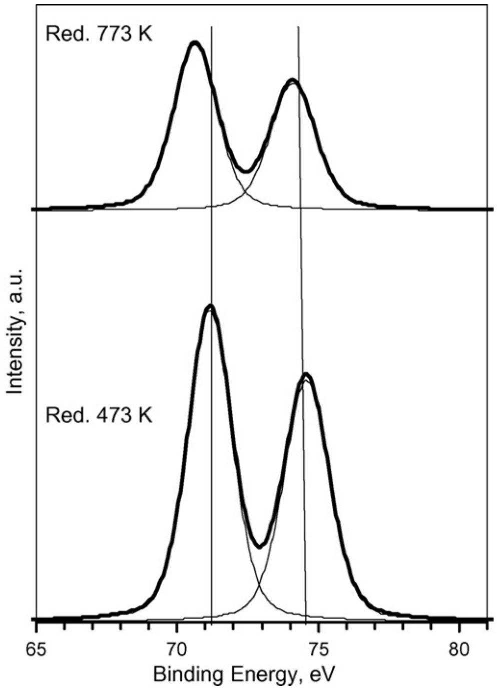

Fig. 1. XPS Pt 4f spectra of the reduced S-PtSn/TiO_2 (2:1) catalyst.

The Sn $3d_{5/2}$ spectra for the catalysts reduced at 473 and 773 K are plotted in Fig. 2. The spectra show a shift in the binding energy towards lower values with increasing reduction temperature, thus indicating the reduction of oxidized tin species. One or two bands appear when the catalysts are reduced at 473 K, which can be ascribed to tin in higher oxidation states. Discrimination between Sn(II) and Sn(IV) species with XPS is difficult, as their binding energies are too close; therefore they have been considered together as ‘‘oxidized tin species’’. The spectra for catalyst S-PtSn/TiO_2 (1:1) shows a small band centred at 484.7 eV which does not appear in the other catalysts after reduction at low temperature. This contribution is attributed to reduced tin [11,38].

Table 1
Catalyst characterization by XPS

Catalyst	Treatment	Pt $4f_{7/2}$ BE (eV)	Sn $3d_{5/2}$ BE (eV)	Pt/Ti	Pt/Sn	Sn_{ox}/Sn_{total}
C-PtSn/TiO_2 (2:1)	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
C-PtSn/TiO_2 (1:1)	Red. 473 K	71.7	485.5–486.6	0.0391	0.509	1
	Red. 773 K	71.3	484.8–486.7	0.0300	0.367	0.85
S-PtSn/TiO_2 (2:1)	Red. 473 K	71.2	486.1	0.0257	0.528	1
	Red. 773 K	70.6	485.0–486.7	0.0125	0.184	0.66
S-PtSn/TiO_2 (1:1)	Red. 473 K	71.2	484.7–486.2	0.0285	0.646	0.96
	Red. 773 K	70.9	485.0–486.7	0.0184	0.194	0.73

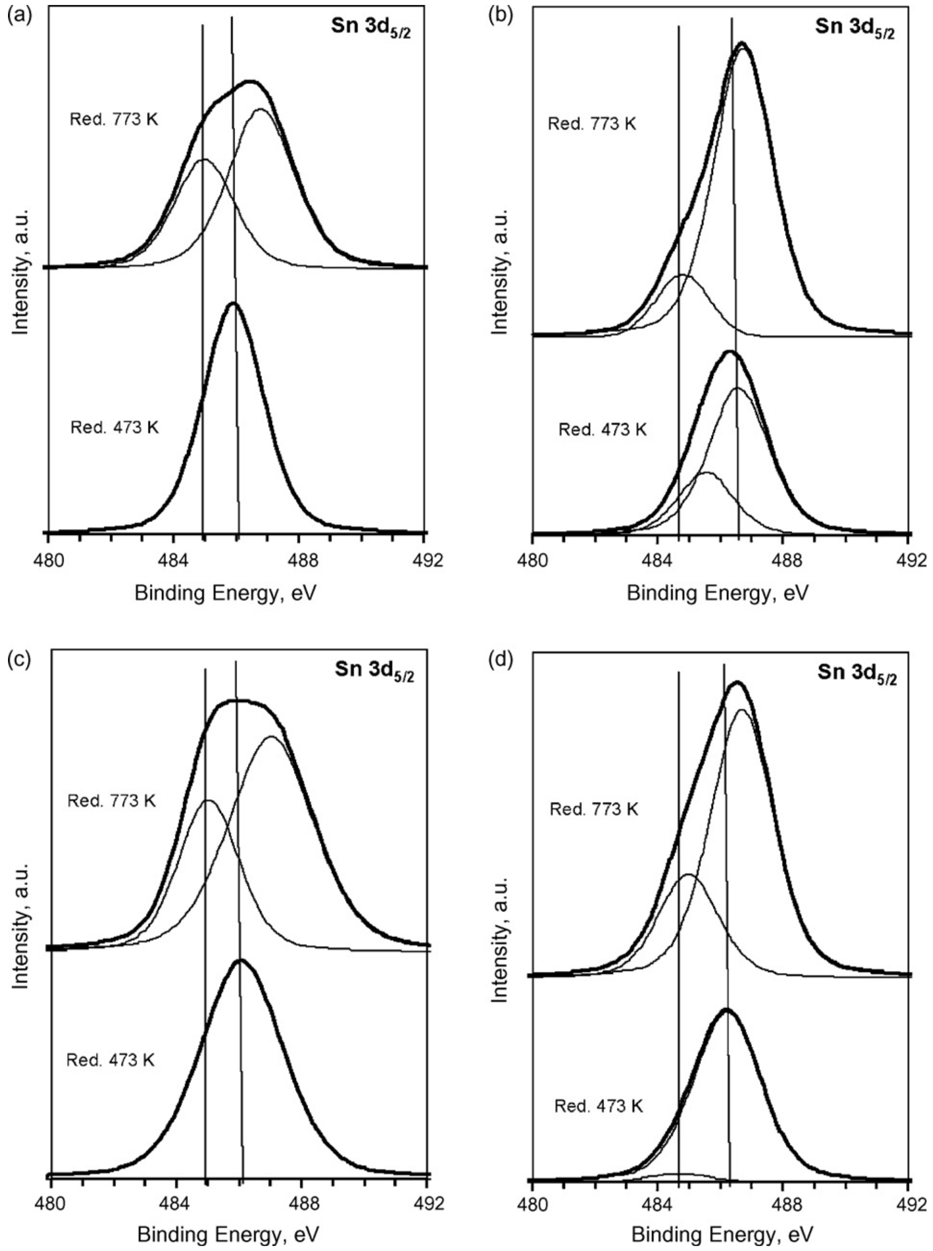

Fig. 2. XPS Sn 3d spectra of the reduced PtSn/TiO_2 catalysts: (a) C-PtSn/TiO_2 (2:1), (b) C-PtSn/TiO_2 (1:1), (c) S-PtSn/TiO_2 (2:1) and (d) S-PtSn/TiO_2 (1:1).

The spectra show a broadening of the Sn $3d_{5/2}$ peaks with an increase in reduction temperature, with the appearance of a shoulder at low binding energies. This facilitated deconvolution of the experimental spectra into two peaks; one at low binding energy values, assigned to metallic tin, and the other one at higher binding energies, attributed to oxidized tin species. 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 an 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 bimetallic Pt–Sn phases after this treatment, although this cannot be readily assessed by XPS.

After reduction at both temperatures, the Pt/Ti atomic ratio of the catalysts decreases as the amount of tin decreases (see Table 1). On the other hand, a decrease in this ratio is also observed when the reduction temperature is increased for a given catalysts that can be assigned to three main effects: (i) dilution of platinum by metallic tin, upon the formation of Pt:Sn bimetallic phases, (ii) covering of metal particles surface by oxidized tin species and (iii) formation of partially reduced titanium oxide, TiO_{2-x}, that can migrate onto the surface of the metallic particles leading to partial decoration. By comparing the different methods of preparation, it can be concluded that higher dispersions are obtained, as determined by XPS, with the coimpregnation method.

The Pt/Sn ratio decreases when the amount of tin increases, and also after reduction at high temperature, which can be

Table 2
CO uptake and CO/Pt ratios for catalysts reduced at both 473 and 773 K

Catalyst	Treatment	CO uptake (μmol g^{-1})	CO/Pt
C-PtSn/TiO_2 (2:1)	Red. 473 K	18	17.6
	Red. 773 K	13	12.7
C-PtSn/TiO_2 (1:1)	Red. 473 K	41	40.0
	Red. 773 K	12	11.7
S-PtSn/TiO_2 (2:1)	Red. 473 K	21	20.5
	Red. 773 K	13	12.7
S-PtSn/TiO_2 (1:1)	Red. 473 K	17	16.6
	Red. 773 K	13	12.7

attributed to the effects previously discussed. After reduction at high temperature, catalysts prepared by successive impregnation have a higher surface enrichment with tin species, which probably indicates a close proximity between platinum and tin, this favouring surface enrichment with tin species. On the other hand, the surface Pt:Sn atomic ratio is, in all cases, lower than the bulk one, thus indicating a surface segregation of tin species.

The ratio between the oxidized tin species and the total amount of tin (Sn_{ox}/Sn_{total}) shows that tin is all in an oxidized state after reduction at 473 K, except for the S-PtSn/TiO_2 (2:1) catalyst where a small amount, *ca.* 4%, is in a metallic state. After reduction at 773 K, a fraction of tin is in the metallic state. The extent of tin reduction strongly depends on the preparation method in samples with Pt:Sn atomic ratio of 1:1, for which the sample prepared by the successive impregnation method has a higher amount of metallic tin suggesting a greater extent of interaction with platinum.

3.2. CO adsorption microcalorimetry

Table 2 reports the CO/Pt ratios obtained from CO adsorption at room temperature on the different catalysts. These values have been calculated by taking into account the total platinum loading and assuming that no CO is adsorbed on tin sites, as well as the CO uptake deduced from the amount of CO adsorbed with a heat of adsorption higher than 40 kJ/mol. Fig. 3 shows the differential heat of CO adsorption as a function of the coverage at 298 K for catalysts reduced at 473 K. The profiles for all catalysts are very similar. The initial heat of adsorption is about 125 kJ/mol, but when the CO coverage increases the value decreases, reaching a plateau at around 100 kJ/mol. The constant value of the plateau extends over a wide range of coverage. At higher coverage there is a drastic decrease in the differential heat of adsorption, which indicates a saturation of the surface sites. The high initial heat of adsorption can be attributed to a small amount of CO adsorbed on low coordinated platinum atoms, as corners or edges [39], and the plateau indicates an energetic homogeneity of the metal atoms, giving a slight decrease in the heat of adsorption with coverage, probably arising from interactions between neighbouring CO molecules [40].

The CO uptakes for PtSn/TiO_2 (2:1) catalysts are similar (Table 2), being slightly higher for the catalyst prepared by successive impregnation. However, between the PtSn/TiO_2 (1:1) catalysts, the CO uptake for the catalyst prepared by coimpregnation is more than twice that of its counterpart prepared by successive impregnation. Chemisorption data are not in good agreement with the Pt/Ti XPS atomic ratios (Table 1), and these results could be explained by a partial coverage of the metal particle surface by a thin layer of tin oxide species. This thin layer would allow the photo-electrons emitted from the underlying platinum atoms to be detected.

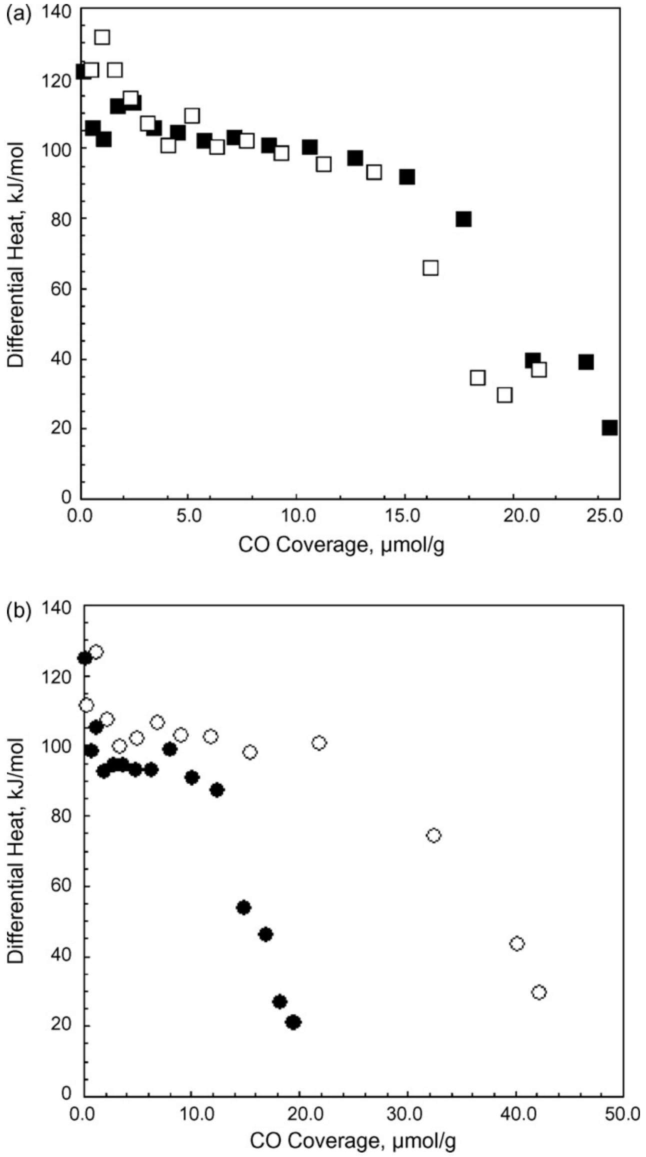

Fig. 3. Differential heats of CO adsorption as a function of the adsorbate coverage at 298 K on (a) PtSn/TiO_2 (2:1) and (b) PtSn/TiO_2 (1:1) prepared by coimpregnation (□, ○) and successive impregnation (■, ●) after reduction at 473 K.

Different differential heat of adsorption profiles are obtained after reduction at high temperature (Fig. 4). Catalysts with a Pt:Sn atomic ratio of 2:1 showed similar heat-coverage profiles, the initial heat of adsorption being about 140 kJ/mol, and the heat of adsorption strongly decreasing with coverage, thus indicating a heterogeneous distribution of active sites. The saturation coverage for CO adsorption decreases when the

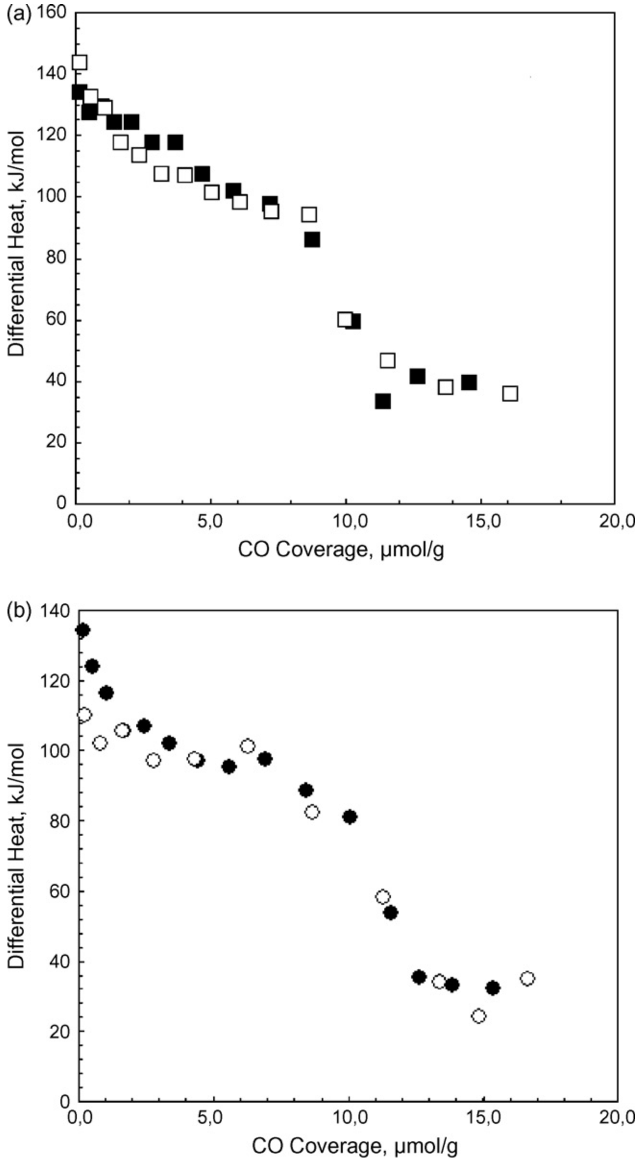

Fig. 4. Differential heats of CO adsorption as a function of the adsorbate coverage at 298 K on (a) $PtSn/TiO_2$ (2:1) and (b) $PtSn/TiO_2$ (1:1) prepared by coimpregnation (□, ○) and successive impregnation (■, ●) after reduction at 773 K.

reduction temperature increases (Table 2), which correlates with the atomic Pt/Ti ratios obtained by XPS. This loss in adsorption capacity can be associated with the migration of partially reduced titania particles to the platinum surface and a diluting effect by formation of Pt:Sn bimetallic phases.

Catalysts with Pt:Sn atomic ratio of 1:1 reduced at 773 K show different heat-coverage profiles depending on the preparation method. Whereas the catalyst prepared by successive impregnation has the same profile than catalysts discussed previously, the catalyst prepared by coimpregnation has a lower initial heat of adsorption (110 kJ/mol), which was maintained until saturation of the surface. This suggests a higher homogeneity of the surface metal atoms for CO adsorption than their counterparts after reduction at high temperature. The CO uptake decreases when compared with catalysts reduced at 473 K, which is ascribed to the effects previously discussed.

It is important to remark that the CO uptake (*ca.* 13 μmol g^{-1}) is similar for all catalysts reduced at high temperature, and that it is independent of both the amount of tin and the preparation method.

3.3. Infrared spectroscopy

Fig. 5 compares the FTIR spectra of CO adsorbed at room temperature on the $PtSn/TiO_2$ catalysts, after *in situ* reduction at 473 K. In all cases, catalysts were exposed at 298 K to increasing CO doses until reaching 50 Torr, followed by evacuation under high vacuum for 1 h at 298 K. All spectra exhibit bands in the 2150–2000 cm^{-1} region, which are assigned to CO linearly adsorbed on the different metallic sites [41,42]. For $PtSn/TiO_2$ (2:1) catalysts (Fig. 5a), the spectrum obtained after introduction of a CO dose of less than 0.1 Torr contains only a broad band centred at 2073 cm^{-1} and a shoulder around 2040 cm^{-1}. An increase in the CO pressure produces a blue shift of the main band, which is at 2083 cm^{-1} at the highest coverage, as well as an increase in the intensity of all bands. The

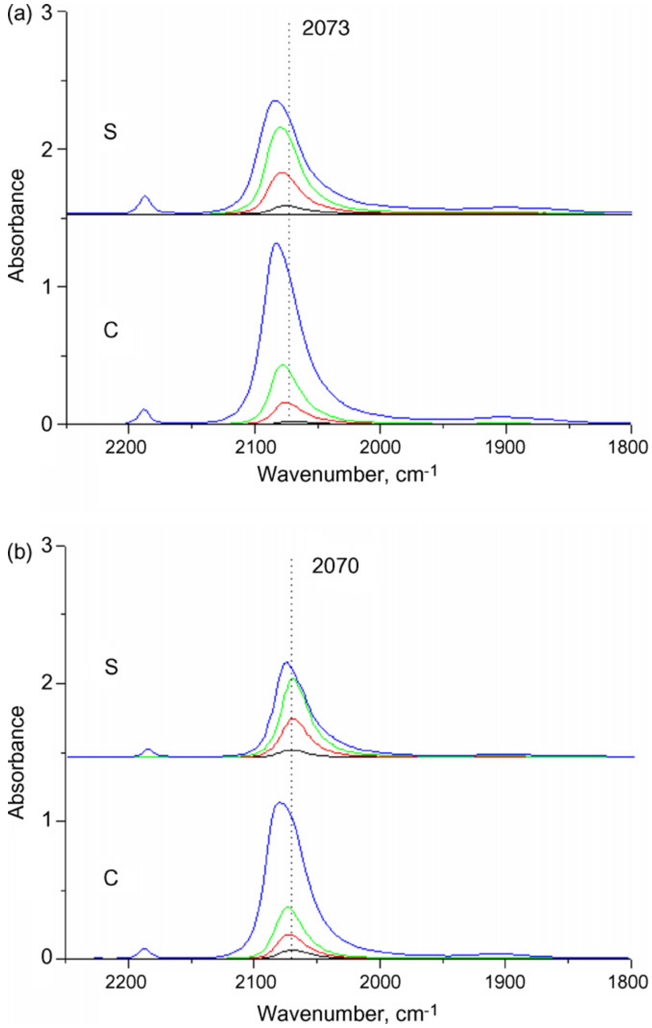

Fig. 5. IR spectra of $PtSn/TiO_2$ catalysts with Pt:Sn atomic ratio of (a) 2:1 and (b) 1:1, prepared by coimpregnation (C) and successive impregnation (S) after reduction at 473 K and exposed to <0.1 Torr (▬), 0.1 Torr (▬), 0.2 Torr (▬) and 50 Torr (▬) CO at 298 K.

bands are 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 broad band is observed at 1900 cm^{-1} due to bridge-bonded CO. There is also a band centred at 2188 cm^{-1}, which is assigned to CO adsorbed on the support [43], and which readily disappears after evacuation at 298 K.

The FTIR spectra of $PtSn/TiO_2$ (1:1) catalysts reduced at 473 K (Fig. 5b) showed the same features as those discussed previously, although the greater amount of tin produced a shift to lower band positions for CO on linear sites (to 2070 cm^{-1} at low coverage and 2078 cm^{-1} at the highest coverage). The band attributed to bridge-bonded CO was less prominent for catalysts with a higher amount of tin.

After reduction at 773 K, the band due to linearly adsorbed CO is detected at lower wavenumbers when compared to catalysts reduced at 473 K (Fig. 6). Spectra of $PtSn/TiO_2$ (2:1) catalysts showed, at low coverage, a maximum in intensity at 2065 cm^{-1}. As in the previous spectra, it is followed by a shoulder at 2040 cm^{-1}. At the highest coverage, the band is blue shifted to 2080 and 2072 cm^{-1} for the coimpregnation and successive impregnation catalysts, respectively. Bands at lower wavenumbers were found for CO adsorption on $PtSn/TiO_2$ (1:1) catalysts, the bands being centred at 2056 and 2062 cm^{-1} for coimpregnation and successive impregnation catalysts, respectively, at low coverage, and 2066 at the highest coverage.

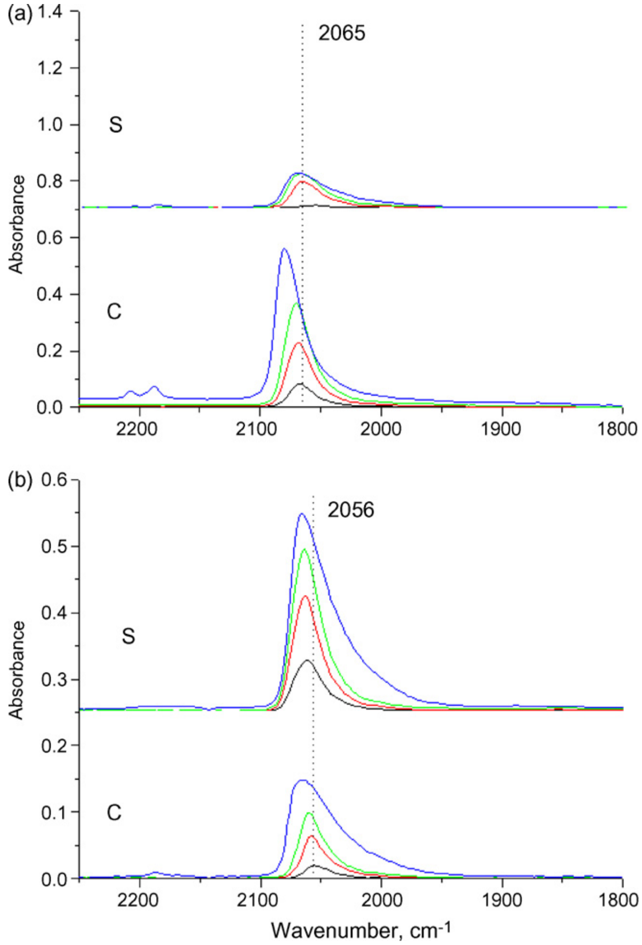

Fig. 6. IR spectra of $PtSn/TiO_2$ catalysts with Pt:Sn atomic ratio of (a) 2:1 and (b) 1:1, prepared by coimpregnation (C) and successive impregnation (S) after reduction at 773 K and exposed to <0.1 Torr (▬), 0.1 Torr (▬), 0.2 Torr (▬) and 50 Torr (▬) CO at 298 K.

The band due to bridge-bonded CO was not detected after reduction at high temperature. Nevertheless, two bands appear at high CO coverage, at 2208 and 2188 cm^{-1}, which correspond to CO adsorbed on partially reduced titania and unreduced titania, respectively. These bands disappear after evacuation under vacuum at 298 K.

Comparing these results with previous studies on monometallic Pt/TiO_2 catalysts [43,44] after reduction at 473 K, it can be concluded that the effect of tin addition was to shift the dominant band due to CO linearly adsorbed to lower wavenumbers, and this is consistent with previous results on $PtSn/Al_2O_3$ catalysts [45,46]. Bands can be assigned by reference to single crystal studies and by considering coordination number and the number of neighbouring sites likely to result in coupling interactions [42,47,48]. The highest wavenumber band observed can be attributed to CO linearly adsorbed on terrace sites with low extension or where the metal atoms are in a less dense close packing arrangement such as in (1 0 0) facets. These results can be rationalised by a geometric effect, assuming that tin oxide species are partially covering the surface of the particles of platinum, thus reducing the coupling interactions between molecules adsorbed on terraces. The contribution at 2040 cm^{-1} probably reflects sites located at edges and kinks [41,42,47,49].

The band at 1900 cm^{-1} appears at a high wavenumber for bridged CO on Pt catalysts [41,50]. This effect can be ascribed to the influence of Cl-adatoms from the metallic precursors for Pt_2CO involving adjacent pairs of reduced Pt atoms which have been rendered cationic by e-withdrawal [46]. The intensity of the band decreases with the amount of tin loaded, suggesting the presence of tin species on exposed platinum surface that can block bridging Pt–Pt sites.

The spectra were similar for all catalysts reduced at 473 K. However, in the case of S-$PtSn/TiO_2$ (1:1) catalysts, the band of linearly adsorbed CO does not shift to higher wavenumbers when the coverage is increased (Fig. 6b). This would be consistent with a geometric effect due to the formation of a Pt–Sn alloy phase. This tin in a metallic state would make a dilution of the surface platinum atoms, removing the number of dipolar coupling interactions of each Pt–CO [45,51]. This would be in agreement with XPS results, where a small part of tin in metallic state was detected.

After reduction at 773 K (Fig. 6), as in the catalyst discussed previously, the band attributed to linearly adsorbed CO was not shifted with increasing coverage, which suggest that CO is adsorbed at platinum sites in the surface of Pt–Sn alloy particles [45,52]. Nevertheless, a shift to higher wavenumbers is observed at high coverage, therefore, not all the surface platinum are involved in forming the Pt:Sn alloy phase(s). For catalysts prepared by coimpregnation the shift is greater, which suggests that a higher proportion of unalloyed platinum is present as compared to successive impregnation catalysts. These results were accompanied by a red shift of the band position when compared to the catalysts reduced at 473 K. This is consistent with an electronic effect, where the platinum in Pt–Sn alloy is less electron deficient than free platinum [53,54]. Therefore, tin addition should contribute to a shift of the band to lower wavenumbers.

A decrease in the band intensities is also observed after reduction at 773 K, as well as the disappearance of the band corresponding to bridge-bonded CO. The former observation correlates with the decrease observed in the CO chemisorption capacity; it cannot be ascribed to the sintering of metal particles, as larger particles would yield a higher proportion of CO adsorbed on close packed terrace sites, resulting in a shift to higher wavenumbers and a blue shift with increasing CO coverage due to dipolar coupling effects [45]. XPS results have shown that, upon reduction at high temperature (773 K), both the Pt/Ti and the Pt/Sn surface atomic ratios decrease with regard to those obtained after reduction at low (473 K) temperature. Furthermore, a given amount of oxidized tin species is reduced to metallic tin, this opening the possibility to the formation of Pt–Sn alloys. Thus, the observed results (lower intensity of IR CO bands and lose of bridge-bonded CO after reduction at 773 K) can be assigned to a combination of at least, three facts: (i) migration of partially reduced titania to the surface of metallic particles, (ii) covering of metal particle by oxidized tin, and (iii) dilution of surface platinum atoms by the formation of Pt–Sn alloy phases.

3.4. Crotonaldehyde hydrogenation

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 catalysts reduced at 473 K is plotted in Fig. 7a. Data are reported after carbon balance was achieved, since no reliable data can be assessed when reactant and products were adsorbed during the initial stages of the reaction. The behaviour was similar in all cases; the activity drastically decreases during the first 25–50 min, thereafter remaining practically stable as a function of time on stream. Catalysts prepared by coimpregnation have the highest activities, following the order C-PtSn/TiO_2 (1:1) > C-PtSn/TiO_2 (2:1) > S-PtSn/TiO_2 (2:1) > S-PtSn/TiO_2 (1:1) where the activities at the end of the reaction are considered.

In all cases, reduction at 773 K produces an increase in activity (Fig. 8a), as reported in the literature [11]. It is important to remark that for catalysts with a higher tin loading, PtSn/TiO_2 (1:1), the increase in activity is greater. Comparing activities at the end of the reaction, the activities are 15.7 and 8.3 times higher than after reduction at 473 K for C-PtSn/TiO_2 (1:1) and S-PtSn/TiO_2 (1:1) catalysts, respectively, and 5.4 and 1.6 times higher for catalysts C-PtSn/TiO_2 (2:1) and S-PtSn/TiO_2 (2:1), respectively.

Taking into account the XPS, CO chemisorption and FTIR data, reduction at 773 K causes a decrease in the number of surface active sites. This suggests that the remaining surface platinum atoms are much more active. The presence, after reduction at high temperature, of tin oxide and partially reduced patches of titania decorating surface platinum particles, and the formation of Pt–Sn alloy, suggested by FTIR, were potential reasons for the promoting effect after reduction at high temperature. Tin oxide and partially reduced titania act as electrophilic centres or Lewis acid sites interacting with the oxygen atom of the carbonyl function, and this interaction weakens the C=O bond, that becomes more reactive toward hydrogenation [31,55]. On the other hand, a change in the electronic state of platinum is induced by alloying with tin, and this change influences the bond strength between the bond adsorbed species and the surface [56]. It was reported that such hydrogenation reactions occurred faster on surface with decreased electron density [57].

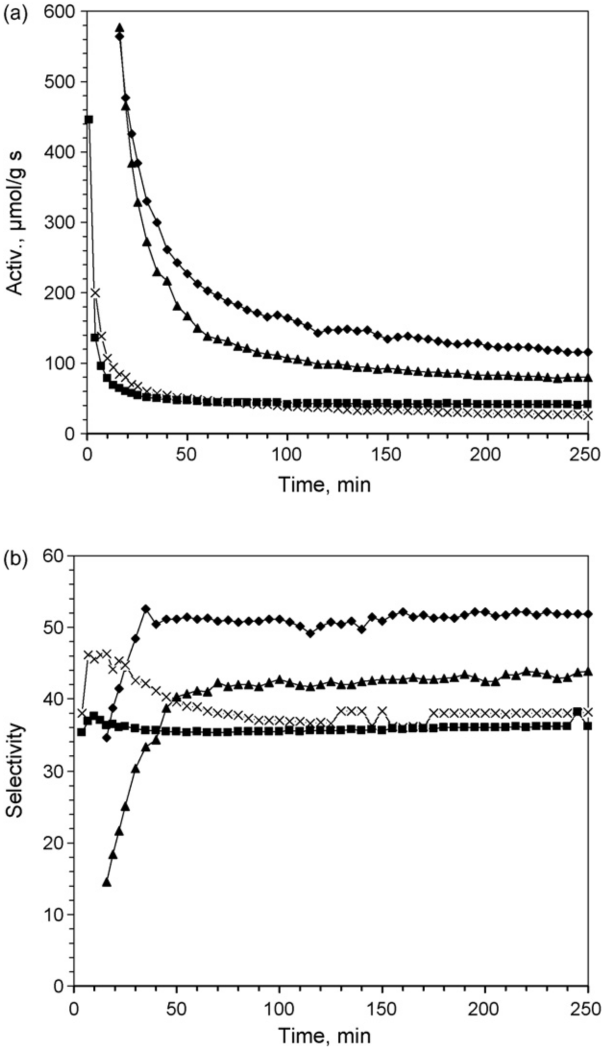

Fig. 7. Evolution of (a) activity and (b) selectivity toward crotyl alcohol for crotonaldehyde hydrogenation with time on stream at 333 K for C-PtSn/TiO_2 (2:1) (▲), C-PtSn/TiO_2 (1:1) (◆), S-PtSn/TiO_2 (2:1) (■) and S-PtSn/TiO_2 (1:1) (×) catalysts reduced at 473 K.

In the hydrogenation of crotonaldehyde, a molecule containing two conjugated double bonds, two primary hydrogenation routes can take place: (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.

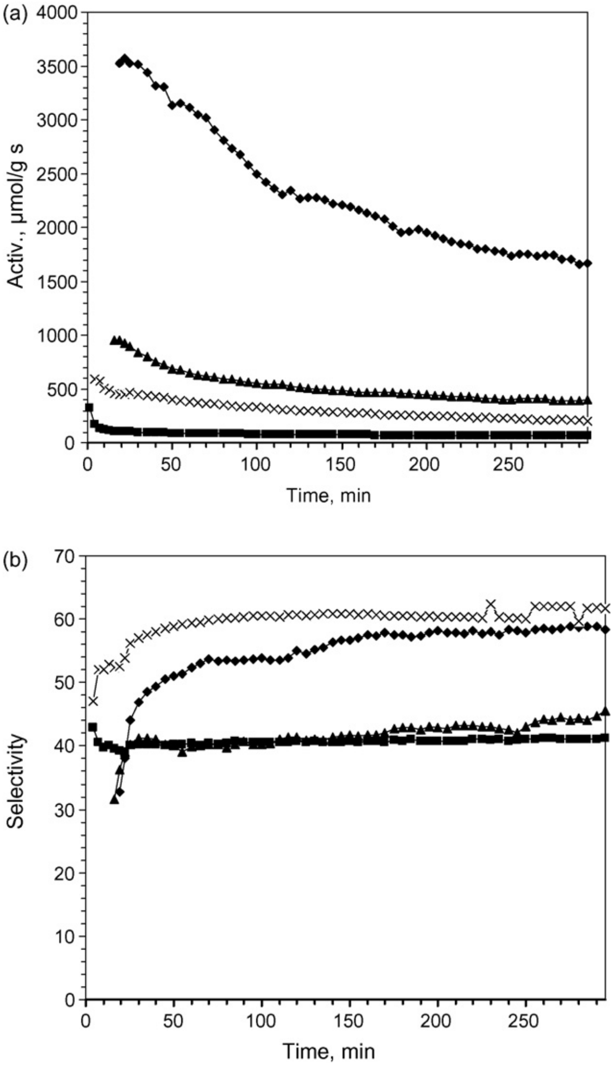

Fig. 8. Evolution of (a) activity and (b) selectivity toward crotyl alcohol for crotonaldehyde hydrogenation with time on stream at 333 K for C-PtSn/TiO_2 (2:1) (▲), C-PtSn/TiO_2 (1:1) (◆), S-PtSn/TiO_2 (2:1) (■) and S-PtSn/TiO_2 (1:1) (×) catalysts reduced at 773 K.

Moreover, decarbonylation and cracking could also take place, yielding light hydrocarbons (C_{1-3}). The extend of the secondary reactions depends on the total conversion; therefore, the selectivity toward crotyl alcohol usually decreases when the conversion increases [12,14,30].

In this study, the only reaction products detected were butanal, crotyl alcohol and a small amount of butane and butanol. Fig. 7b compares the selectivity toward crotyl alcohol as a function of time on stream for the PtSn/TiO_2 catalysts reduced at 473 K. For catalysts prepared by successive impregnation, the selectivity remains constant with the time on stream, whereas for catalysts prepared by coimpregnation there is an increase in selectivity during the first minutes of reaction, reaching a nearly constant value. This may be because at the first minutes of reaction, the conversion is very high, and a given part of crotyl alcohol is hydrogenated to butanol.

Selectivity towards crotyl alcohol after reduction at 473 K has a strong dependence on the preparation method. Whereas selectivity for catalysts prepared by the successive impregnation method was similar in both cases (around 37%), a higher value was obtained for catalysts prepared by coimpregnation (44 and 52% for C-PtSn/TiO_2 (2:1) and C-PtSn/TiO_2 (1:1), respectively). Bearing in mind that after this treatment no SMSI effect is expected, and that Pt–Sn alloy formation was not detected by XPS and IR spectroscopy, a greater amount of oxidized tin species on the metal particles is suggested to account for this promoting effect. Oxidized tin species, which interact with the oxygen atom of the carbonyl bond, can weaken the bond and favour hydrogenation.

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. 8b). The selectivity toward crotyl alcohol remains practically constant with time on stream. For all catalysts, the selectivity towards crotyl alcohol was increased as compared to that obtained when catalysts were reduced at low temperature (473 K), except for the catalyst with atomic ratio Pt:Sn = 2:1, for which the selectivity remained practically constant. First, the enhancement in the selectivity toward crotyl alcohol could be explained by the formation of new sites at the metal-partially reduced titania support and metal–tin oxidized species that activate the carbonyl bond and favour hydrogenation. On the other hand, the creation of Pt–Sn alloy would decrease the number of sites which are able to hydrogenate the C=C bond. These sites are unmodified or slightly modified platinum ensembles, and the formation of Pt–Sn alloy would destroy them, slowing down the rate of C=C hydrogenation [14].

In this case, the selectivity toward crotyl alcohol is not affected by the preparation mode, but it increases with the amount of tin (Fig. 8b), which reveals the important role of both the formation of Pt–Sn alloy and the existence of oxidized tin species on the platinum particles, although it cannot be clearly assessed which effect is more relevant for the selectivity toward crotyl alcohol.

The overall conversion was held within the range from 2 to 10%. Nevertheless, there are no important changes in the selectivity towards crotyl alcohol with conversion.

4. Conclusions

This study compares the catalytic behaviour of PtSn/TiO_2 catalysts prepared by successive impregnation or coimpregnation on the selective hydrogenation of crotonaldehyde after reduction at 473 and 773 K. Results show a pronounced influence of the method of preparation on the catalytic properties. The catalysts prepared by coimpregnation have higher activities and selectivities toward crotyl alcohol than their counterparts prepared by successive impregnation after reduction at 473 K, which is attributed to the presence of oxidized tin species on the surface of the metal particles. XPS, CO chemisorption and infrared results show that reduction at 773 K decreased the number of exposed platinum sites, but activities and selectivities were improved. The decoration of platinum particles with partially reduced titania and oxidized tin species, and the formation of Pt–Sn alloy are suggested as the origin of these effects. As in the case of reduction at low temperature, the activity of catalysts prepared by coimpregnation was also higher after reduction at 773 K although in this case, the selectivity toward crotyl alcohol was not affected by the preparation mode. However, the selectivity was increased with tin loading, which reveal the importance of tin in these systems both in the oxidized and in the metallic states.

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