

# Vapor-Phase Hydrogenation of Crotonaldehyde on Titania-Supported Pt and PtSn SMSI Catalysts

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Vapor-phase hydrogenation of toluene and selective hydrogenation of crotonaldehyde have been performed after reduction at low (523 K) and high (773 K) temperatures over Pt/TiO<sub>2</sub> and PtSn/TiO<sub>2</sub> catalysts prepared from the metal precursors tin(II) oxalate and H<sub>2</sub>PtCl<sub>6</sub>. A sequential impregnation method was used to prepare the bimetallic catalyst, wherein the tin precursor was loaded first. The surface characteristics of both catalysts were evaluated with X-ray photoelectron spectroscopy (XPS) after the reduction treatments. It was shown in this analysis that tin was mainly in an oxidized state in the bimetallic catalyst (about 80%) even after reduction at 773 K. The presence of tin and the increase in the reduction temperature strongly decreased the catalytic activity for toluene hydrogenation, but the opposite effect was observed for crotonaldehyde hydrogenation. After reduction at low temperature, the bimetallic catalyst was more active than the monometallic catalyst, but it was less selective toward hydrogenation of the carbonyl bond to yield the unsaturated alcohol. However, reduction at 773 K yielded a bimetallic catalyst that showed an initial activity five times higher than that of the Pt/TiO<sub>2</sub> catalyst reduced at the same temperature and a high selectivity (around 50%) toward the unsaturated alcohol, which was stable with time on reaction. Furthermore, the catalytic behavior of the bimetallic catalysts was also evaluated after reduction at even higher temperatures. Reduction at 873 K increased the catalytic activity in crotonaldehyde hydrogenation while the selectivity to crotyl alcohol remained at about 50% molar fraction; however, reduction at 973 and 1023 K caused a loss of catalytic performance in terms of both activity and selectivity. © 2002 Elsevier Science (USA)

**Key Words:** SMSI; Pt/TiO<sub>2</sub>; PtSn/TiO<sub>2</sub>; crotonaldehyde hydrogenation.

## INTRODUCTION

The modification of the catalytic properties of a dispersed metal by the support was first reported by Schwab and Schultes (1). Their studies gave rise to a vast amount of research trying to find both explanations and new catalytic applications. The main part of the earlier findings on this subject were reviewed by Schwab (2) and Solymosi (3). In the late seventies, Tauster *et al.* (4, 5) found that, when used

as supports, partially reducible oxides such as TiO<sub>2</sub> could modify the chemisorption behavior 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. Furthermore, it was demonstrated that this interaction could also modify the activity and selectivity of noble metals in different reactions, such as those involving molecules containing carbonyl bonds. Vannice and co-workers (6) showed that the activity for CO methanation was much higher for Pd/TiO<sub>2</sub> in the SMSI state than for palladium supported on silica, alumina, or silica–alumina, and that the same ranking was valid for platinum-based catalysts. They also observed that the CO coverage during reaction conditions was very small on Pt/TiO<sub>2</sub> in the SMSI state despite its higher activity (7). At that time, this was attributed to a weakened CO–metal bond, which resulted in a more competitive hydrogen chemisorption and higher surface concentrations of hydrogen under reaction conditions.

The research work carried out during the past years has offered a series of explanations for this distinctive behavior. An electronic effect of titania on supported nickel was already proposed by Szabó and Solymosi (8). More recently, Horsley (9) and Tauster *et al.* (10) assumed an electron transfer from titania to the supported metal to explain the SMSI phenomenon. A similar conclusion was drawn by Herrmann (11) after following the electrical conductivity of Pt, Rh, and Ni catalysts supported on TiO<sub>2</sub> during different reduction treatments at low (473 K) or high (773 K) temperatures in H<sub>2</sub>. Resasco and Haller (12) proposed a model involving a delocalized transfer of charge from the metal to TiO<sub>2</sub> after low-temperature reduction and a localized transfer of charge from the support to the metal after high-temperature reduction. Additionally, these authors suggested that migration of reduced species from the support onto the metal particles occurred after high-temperature reduction (13). This latter model (geometrical effect) would explain the decrease in the H<sub>2</sub> and CO chemisorption ability of the catalysts in the SMSI state, because the amount of surface platinum atoms is diminished. Moreover, the creation of special sites at the metal-support interface, which would be able to activate the carbonyl bond or the CO

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molecule by interaction with the oxygen atom, can explain the enhanced activity of these systems (14). With regards to this, recent studies with high-resolution transmission electron microscopy (HRTEM) have shown the occurrence of metal decoration in Rh/TiO<sub>2</sub> catalysts reduced at 773 K (15–18), and that the reduced titania covering the metal crystallites has an amorphous nature (19). It has also been demonstrated recently that, together with this geometrical effect, the electronic effect also plays its role in the Rh/TiO<sub>2</sub> system and that the onset of the electronic perturbation is observed at a lower reduction temperature than that of the geometric effect (20).

The catalytic behavior of titania-supported noble-metal catalysts after reduction at high temperature has been analyzed in a great number of reactions including the hydrogenation of a carbonyl bond. Thus, in addition to CO hydrogenation (21–23), the hydrogenation of acetone (24), crotonaldehyde (25–27), cinnamaldehyde (28), acetophenone (29), benzaldehyde (30), phenyl acetaldehyde (31), citral (32), and acetic acid (33) have also been reported. In all cases, the turnover frequencies for the hydrogenation of the carbonyl bond obtained with the Pt/TiO<sub>2</sub> catalyst in the SMSI state were much higher than those obtained with the same catalyst reduced at low temperature or with platinum supported on silica or alumina. For molecules where a carbon–carbon double bond is also present in addition to the carbonyl bond (crotonaldehyde, citral, cinnamaldehyde, etc.) a higher selectivity toward the hydrogenation of the C=O bond is obtained, enabling the synthesis of industrially important unsaturated alcohols in high yield. These compounds are important intermediates for the production of perfumes, fragrances, and pharmaceuticals (34), the production of which, through the hydrogenation of unsaturated aldehydes, incurs the problem of easier hydrogenation of the C=C bond, both from the thermodynamic and kinetic points of view, which would lead to the production of saturated aldehydes. Thus, the use of noble metals supported on titania or other reducible oxides (35), after reduction at high temperature (about 773 K), for the selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to obtain unsaturated alcohol is a very promising field in catalysis.

Another group of catalysts that have also shown their applicability for the aforementioned reaction are those based on a noble metal (Pt, Ru) together with a more electropositive metal (Sn, Ge, Zn, etc.). Among them, PtSn catalysts, supported on different materials, have been widely studied (36–45). It has been shown that their performance depends on the Sn/Pt atomic ratio, the preparation method, and, mainly, on the interaction between platinum and metallic and oxidized tin species, and that this interaction can be modified by the choice of an adequate support. However, very few reports can be found on the catalytic behavior of these bimetallic systems supported on partially reducible oxides in the selective hydrogenation of unsaturated

aldehydes. Da Silva and co-workers (28) studied the effect of metal-support interaction in the liquid-phase selective hydrogenation of cinnamaldehyde to cinnamyl alcohol on a PtSn/TiO<sub>2</sub> catalyst with 4 wt% Pt and 0.8 wt% Sn, although the reduction temperature that was used, 423 K, was too low to induce the SMSI effect.

This paper compares the catalytic behavior of titania-supported bimetallic PtSn with monometallic Pt catalysts when subjected to both low (523 K) and high (773 K) reduction temperatures in the vapor-phase hydrogenation of toluene as a structure-insensitive reaction, with that of crotonaldehyde. The surface characteristics of the reduced catalysts have been analyzed by X-ray photoelectron spectroscopy (XPS) to try to correlate the surface characteristics of the catalysts with their catalytic behavior in the aforementioned reactions.

## EXPERIMENTAL

The TiO<sub>2</sub> support used in this study was a nonporous Degussa P25 (60% anatase, 40% rutile), with a surface area of 50 m<sup>2</sup> g<sup>-1</sup> (N<sub>2</sub>, 77 K, BET method). It was calcined in air at 773 K for 4 h prior to catalyst preparation. The bimetallic catalyst, PtSn/TiO<sub>2</sub>, was prepared by sequential impregnation. First, tin was loaded by incipient wetness impregnation of the support with an aqueous solution of tin oxalate (Aldrich) of the appropriate concentration to load 1 wt% tin. Then the sample was dried overnight at 383 K and was subsequently impregnated with an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O (Johnson Matthey). Finally, the solid was dried in an oven at 383 K and stored in a desiccator until use. The platinum content of this bimetallic catalyst was 0.5 wt%, which resulted in a Pt/Sn atomic ratio of 0.32. The monometallic catalyst, Pt/TiO<sub>2</sub>, was prepared in a similar way but without the Sn impregnation step. Its platinum content was 0.7 wt% determined by ICP analysis.

XPS spectra were acquired with a VG-Microtech Multi-lab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg K $\alpha$  ( $h\nu = 1253.6$  eV,  $1$  eV =  $1.6302 \times 10^{-19}$  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 pretreatment chamber and reduced in H<sub>2</sub> for 1 h at 523 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 ca.  $5 \times 10^{-9}$  mbar was reached. The spectra were collected at 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. All binding energies were referenced to the Ti 2p<sub>3/2</sub> line in TiO<sub>2</sub> at 458.5 eV, which provided binding energy values with an accuracy of  $\pm 0.2$  eV. The surface Pt/Ti, Cl/Ti, and Pt/Sn atomic ratios were estimated from

the integrated intensities corrected by the atomic sensitivity factors (46).

The catalytic behavior of the samples in the vapor-phase hydrogenation of toluene or crotonaldehyde (2-butenal) was tested in a microflow reactor at atmospheric pressure under differential conditions. Before the determination of their catalytic behaviors, the catalysts (between 0.05 and 0.15 g) were reduced *in situ* at 523 or 773 K under flowing hydrogen ( $50 \text{ cm}^3 \text{ min}^{-1}$ ) for 4 h and then cooled under hydrogen to the desired reaction temperature. Toluene hydrogenation was studied at 333 K, with a reactant mixture containing purified hydrogen and toluene (Aldrich, HPLC grade) in a  $\text{H}_2/\text{C}_7\text{H}_8$  ratio of 36. Crotonaldehyde hydrogenation was carried out at 313 K. After the reduction treatment, the catalysts were contacted with a reaction mixture (total flow:  $50 \text{ cm}^3 \text{ min}^{-1}$ ;  $\text{H}_2$ /crotonaldehyde ratio of 26) containing purified hydrogen and crotonaldehyde (Fluka, >99.5%), which was prepared by passing a hydrogen flow through a thermostabilized saturator (293 K) containing the unsaturated aldehyde. The concentration of reactants and products at the outlet of the reactor was determined by online gas chromatography with a Carbowax 20 M 58/90 semicapillary column.

## RESULTS AND DISCUSSION

### XPS Characterization

The binding energies of the Pt  $4f_{7/2}$  and Sn  $3d_{5/2}$  levels for catalysts, both freshly prepared (vacuum treatment at room

TABLE 1

XPS Characterization of Titania-Supported Pt and PtSn Catalysts

| Catalyst              | Treatment  | Pt $4f_{7/2}$              |       | Cl/Ti | Sn $3d_{5/2}$                |       |
|-----------------------|------------|----------------------------|-------|-------|------------------------------|-------|
|                       |            | B.E. (eV)                  | Pt/Ti |       | B.E. (eV)                    | Pt/Sn |
| Pt/TiO <sub>2</sub>   | Fresh      | 72.0 (40.4)<br>74.1 (59.6) | 0.024 | 0.029 | —                            | —     |
|                       | Red. 523 K | 70.7                       | 0.012 | 0.010 | —                            | —     |
|                       | Red. 773 K | 70.5                       | 0.013 | 0.004 | —                            | —     |
| PtSn/TiO <sub>2</sub> | Fresh      | 72.1 (47.1)<br>74.1 (52.9) | 0.017 | 0.046 | 486.3                        | 0.42  |
|                       | Red. 523 K | 70.5                       | 0.010 | 0.014 | 484.7 (20.0)<br>486.2 (80.0) | 0.26  |
|                       | Red. 773 K | 70.5                       | 0.010 | 0.006 | 484.7 (22.0)<br>486.3 (78.0) | 0.21  |

temperature) and reduced *in situ* (hydrogen, 523 or 773 K, 1 h), are reported in Table 1 after referencing them to the Ti  $2p_{3/2}$  binding energy of 458.5 eV. In some cases two values are given, which correspond to the deconvolution of the main peak into two components; when necessary, the contribution of each component to the main peak is reported in brackets. Table 1 also presents the Pt/Ti XPS atomic ratio, which can be considered a measure of the platinum dispersion on the titania support and, for the bimetallic catalysts, the Pt/Sn XPS atomic ratio. Furthermore, the Cl/Ti XPS atomic ratios of the two catalysts following the different reduction treatments are also reported.

The Pt  $4f$  spectra for the fresh and reduced catalysts are compared in Figs. 1a (Pt/TiO<sub>2</sub>) and 1b (PtSn/TiO<sub>2</sub>). For

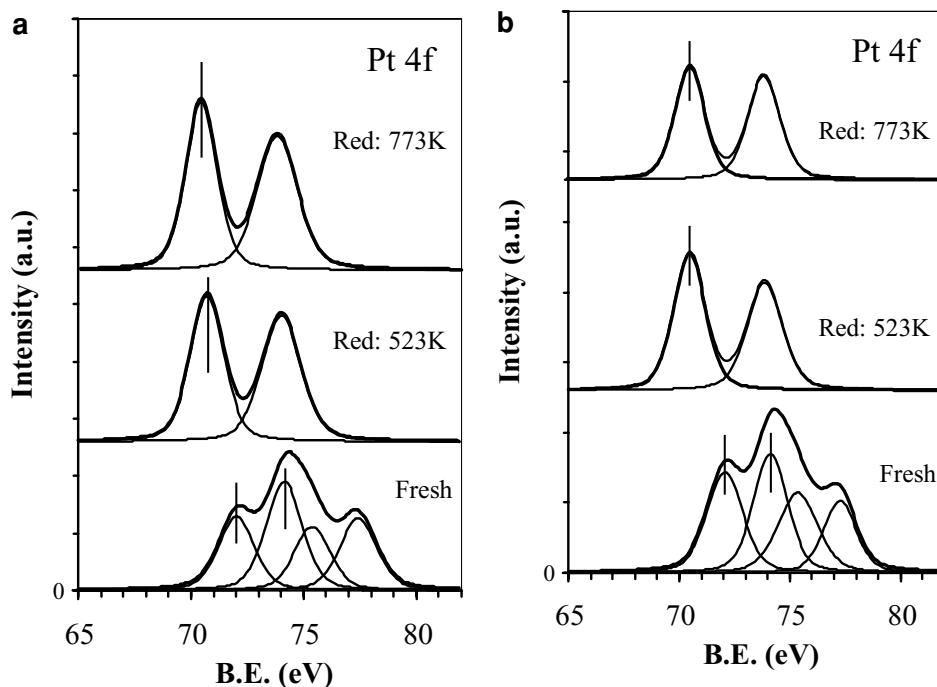


FIG. 1. XPS Pt  $4f$  spectra of the fresh and reduced catalysts: (a) Pt/TiO<sub>2</sub>; (b) PtSn/TiO<sub>2</sub>.

the fresh catalysts, the XPS spectra can be deconvoluted into four peaks, two of them (those placed at lower binding energies) corresponding to the Pt 4f<sub>7/2</sub> level and the others to the Pt 4f<sub>5/2</sub> level. In both catalysts, the peaks arising from the Pt 4f<sub>7/2</sub> level are centered at 72.0–72.1 and 74.1 eV, which are assigned to oxidized platinum species. The exact assignment of these peaks is not easy, because the binding energies of core electrons are affected not only by the metal oxidation state but also by the ligand atoms to which they are coordinated. The binding energy of the Pt 4f<sub>7/2</sub> 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<sub>2</sub>PtCl<sub>6</sub>), but it decreases to 74.8 eV for PtO<sub>2</sub> and further to 74.2 eV for Pt(OH)<sub>4</sub>. Additionally, the binding energy of the Pt 4f<sub>7/2</sub> level for PtCl<sub>2</sub> is reported to be about 73.4 eV, whereas that for Pt(OH)<sub>2</sub> is about 72.4 eV (46). Thus, the XPS analysis of the fresh catalysts reveals that dechlorination of the platinum precursor has taken place, to a certain degree, upon impregnation. In addition, the possibility of a reductive decomposition of the precursor from Pt(IV) to Pt(II) can not be ruled out. In this sense, there are significant differences between the monometallic and the bimetallic catalysts in the fresh state. Regarding the relative contributions of the two deconvoluted peaks to the main peak (Table 1), it can be seen that the contribution of the peak at the higher binding energy (74.2 eV) is less in the bimetallic catalyst. This indicates a higher degree of platinum reduction, from Pt(IV) to Pt(II) species, in the bimetallic catalyst. The different surface chlorine content of both samples also confirms the previous statement. Table 1 lists the Cl/Ti XPS atomic ratios for the fresh catalysts, and it is clear that a higher amount of chlorine remains on the surface of the bimetallic catalyst after impregnation and drying. Furthermore, the Cl/Pt XPS atomic ratio is also higher in the fresh bimetallic catalyst as shown in Fig. 2, which reports the Cl/Pt XPS atomic ratios obtained for the two catalysts after different pretreatments. Therefore, the lower relative intensity of the peak at 74.1 eV in the bimetallic fresh catalyst has to be attributed to the higher degree of partial reduction of Pt(IV) to Pt(II)

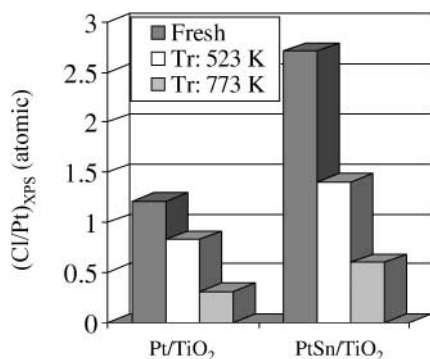


FIG. 2. Cl/Pt XPS atomic ratio in Pt/TiO<sub>2</sub> and PtSn/TiO<sub>2</sub> catalysts.

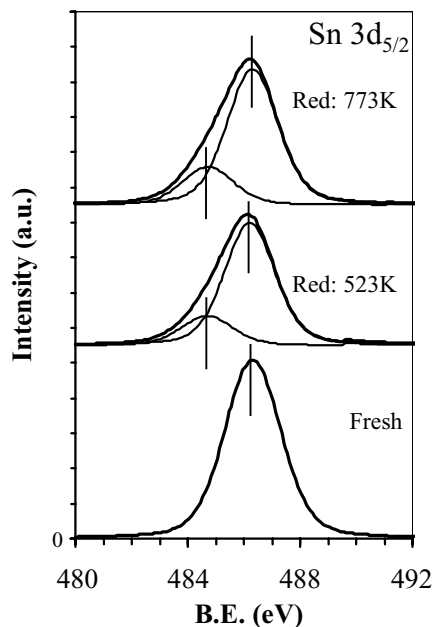


FIG. 3. XPS Sn 3d<sub>5/2</sub> spectra of the fresh and reduced PtSn/TiO<sub>2</sub> catalyst.

species. A similar effect has been observed in the preparation of bimetallic PtSn catalysts supported on pregraphitized carbon black (39). The effect was explained on the basis of a redox reaction between Pt(IV) species and Sn(II) species from the metal precursors which would yield Pt(II) and Sn(IV) species. Unfortunately, the XPS technique cannot be used to discriminate between oxidized tin species.

After reduction at both low (523 K) and high (773 K) temperatures a single peak appears in all cases, centered at about 70.5–70.7 eV, indicating the presence of metallic platinum in the reduced catalysts. On the other hand, the amount of surface platinum strongly decreases with reduction, although it is always lower in the bimetallic catalyst (Table 1 and Fig. 1).

Figure 3 shows the Sn 3d<sub>5/2</sub> spectra obtained for the bimetallic catalyst both in the fresh state and after *in situ* reduction at 523 and 773 K. The spectrum obtained with the fresh catalyst shows a band centered at 486.3 eV, which is characteristic of oxidized tin species. After reduction at 523 K a small contribution centered at 484.7 eV appears, which can be attributed to the presence of metallic tin. Reduction at 773 K produces only a small increase of this contribution, which moves from 20% (reduction at 523 K) to 22% (reduction at 773 K). These results show that the reduction of tin species from the metal precursor is hindered in this catalyst: only a small part of Sn is reduced to the metallic state even after reduction at high temperature (773 K). The reduction degree of tin in bimetallic PtSn catalysts depends on a number of factors, including preparation method, tin precursor, and support used. It has been shown that, for catalysts supported on pregraphitized

carbon black, the amount of metallic tin after reduction at 623 K increases with the tin content in the catalyst in the Sn/Pt atomic range from 0.4 to 1.2, achieving up to 33% Sn<sup>0</sup> (38). Furthermore, different relative amounts of metallic tin were achieved by changing the impregnation method in the preparation of the bimetallic catalysts (39). For bimetallic catalysts supported on alumina and prepared by the reaction of tetrabutyl tin with freshly reduced Pt/Al<sub>2</sub>O<sub>3</sub> samples, percentages of metallic tin ranging from 28 to 63% were achieved after reduction in hydrogen at 723 K, depending on the Sn/Pt atomic ratio (47). A similar wide range has been reported for bimetallic catalysts supported on magnesia prepared with different metal contents but with the same Sn/Pt atomic ratio (close to 1) by using an impregnation method with a methylene chloride solution of the bimetallic complex *cis*-[PtCl(SnCl<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (45). In the case of our PtSn/TiO<sub>2</sub> catalyst, the relatively low amount of metallic tin achieved after reduction even at high temperature (773 K) may be due to a stabilization effect of oxidized tin species by the titania support, which has been reported for catalysts supported on alumina (48–50). It should be noted that nearly the same degree of tin reduction is achieved after treatment at low and high temperature. Thus, the surface composition of the bimetallic catalysts after reduction at 523 and 773 K seems to be very similar, as deduced from XPS analysis. Platinum is in the metallic state whereas tin is both in the metallic and oxidized states, and the proportion between them is very similar. The metallic tin may form an alloy phase with platinum, but that cannot be clearly assessed by XPS.

The increase in the reduction temperature from 523 to 773 K has no effect on the relative amount of surface platinum in both the monometallic and the bimetallic catalysts, as determined by the Pt/Ti XPS atomic ratios (shown in Table 1). This ratio is somewhat higher for Pt/TiO<sub>2</sub>, which can be explained by a dilution effect on platinum surface atoms by tin atoms in the bimetallic PtSn/TiO<sub>2</sub> catalyst. For the latter, the Pt/Sn XPS atomic ratio slightly decreases with the reduction treatment, from 0.26 to 0.21, thus indicating a surface enrichment with tin after reduction at high temperature. However, these differences are not as important to explain as the different catalytic behaviors shown by these catalysts, which are described in the following sections.

### Toluene Hydrogenation

Figure 4 plots the catalytic activity for toluene hydrogenation ( $\mu$ moles of toluene transformed per gram of platinum per second) at 313 K on both the monometallic and the bimetallic catalysts after reduction at low (523 K) and high (773 K) temperatures. For catalysts reduced at low temperature, in which the SMSI effect is not expected, the bimetallic catalyst shows a much lower activity than the monometallic catalyst. Toluene hydrogenation is considered to be a structure-insensitive reaction and, in this way,

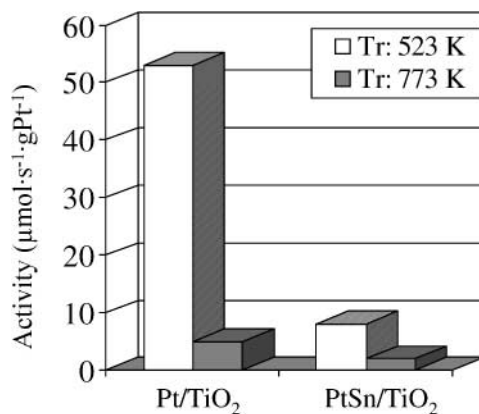


FIG. 4. Catalytic activity for toluene hydrogenation at 313 K of samples Pt/TiO<sub>2</sub> and PtSn/TiO<sub>2</sub> after reduction at low (523 K) and high (773 K) temperature.

the catalytic activity in this reaction should only depend on the number of platinum atoms available at the catalyst surface and would not be affected by the metal particle size or by the crystallographic planes exposed. These results can then be attributed to a dilution effect of tin, which decreases the number of surface platinum atoms available. However, XPS data indicate that the surface Pt/Ti atomic ratio in the monometallic catalyst is not much higher than in the bimetallic catalyst (0.012 vs 0.010). It would then be necessary to account for a negative effect of tin on the hydrogenating behavior of platinum. A similar effect was found in a previous work dealing with PtSn catalysts supported on carbon black (39). It was shown there that addition of a small amount of tin (bulk Pt/Sn ratio: 2.4) caused a decrease in the rate of benzene hydrogenation, that could be related to the decrease of the amount of surface platinum atoms, as obtained by hydrogen and CO chemisorption. However, catalysts with higher amounts of tin (bulk Pt/Sn ratio: 1.2) showed a very low catalytic activity that did not correlate with the loss of surface platinum.

Reduction at 773 K produces a drastic decrease in the catalytic activity for toluene hydrogenation in both catalysts, despite the fact that XPS results do not show any significant modification of the surface Pt/Ti atomic ratio (see Table 1). Reduction at this temperature is known to induce the SMSI effect in titania-supported platinum catalysts, by which oxygen vacancies or coordinatively unsaturated cations are formed, and partially reduced titanium oxide (TiO<sub>2-x</sub>) migrates to decorate platinum crystallites (51). This coverage, with the subsequent decrease of available surface platinum, can be the source of the obtained results, although electronic effects arising from the partially reduced support cannot be ruled out. The fact that XPS can not be used to assess this decoration phenomenon can be related to the low thickness of the TiO<sub>2-x</sub> patches that partially cover the platinum crystallites. If this were so, reduction at high temperature would actually cause a

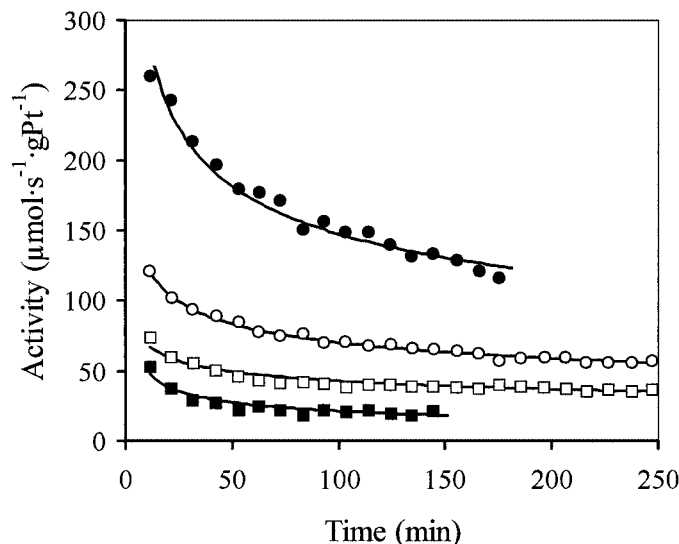


FIG. 5. Evolution of catalytic activity for crotonaldehyde hydrogenation with time onstream at 313 K for catalysts Pt/TiO<sub>2</sub> (■, □) and PtSn/TiO<sub>2</sub> (●, ○) after reduction at 523 K (open symbols) and 773 K (full symbols).

decrease in the amount of surface platinum atoms that cannot be detected by XPS.

### Crotonaldehyde Hydrogenation

Figure 5 plots the evolution of catalytic activity ( $\mu$ moles of crotonaldehyde transformed per second per gram of Pt) as a function of time onstream at 313 K and with a weight-to-flow ratio of  $1.67 \times 10^{-5}$  g s cm<sup>-3</sup>, obtained with the monometallic and the bimetallic catalysts after reduction at both 523 (LRT, low reduction temperature) and 773 K (HTR, high reduction temperature). In the case of the monometallic Pt/TiO<sub>2</sub> catalyst, the increase in the reduction temperature produces a decrease in the catalytic activity per gram of platinum. This result has also been reported by other authors (52), although the most common observation is a strong increase in the turnover frequency (molecules converted per accessible site per second) after catalyst reduction at 773 K (53–55). Reduction at high temperature favors the partial coverage of the platinum crystallites with patches of titanium suboxides (TiO<sub>2-x</sub>). This produces a decrease of the number of accessible platinum surface atoms, but also creates new sites at the metal–oxide interface that are catalytically active for the title reaction. More precisely, these sites are active for the preferential hydrogenation of the carbonyl bond. In this way, it has been proposed that the oxygen atom of the carbonyl function strongly interacts with the Lewis acid sites (coordinatively unsaturated titanium cations) of the partially reduced support. This interaction weakens the C=O bond and thus, the bond becomes more reactive toward hydrogenation (55). Following this model, the observed increase in catalytic activity per surface platinum atom should be accompanied by an increase in the selectivity toward the product of the carbonyl-bond hydro-

genation, crotyl alcohol. The hydrogenation of crotonaldehyde, a molecule containing two conjugated double bonds, can result in a series of products mainly dependent on their individual preferential hydrogenation. The hydrogenation of the olefinic C=C bond yields butanal, whereas the hydrogenation of the carbonyl C=O bond yields crotyl alcohol. These compounds can be further hydrogenated to produce butanol and butane, and crotyl alcohol may also isomerize to butanal. Furthermore, decarbonylation may also take place, yielding C<sub>3</sub> hydrocarbons. The extent of the secondary reactions is determined by the overall conversion, in such a way that selectivity toward crotyl alcohol usually decreases as the conversion degree increases (38, 39, 56).

Under the reaction conditions used in this study, the only products detected were butanal, crotyl alcohol, and a relatively small amount of light hydrocarbons (C<sub>3</sub> and C<sub>4</sub>). Figure 6 compares the evolution of the overall conversion (Fig. 6a) and of the selectivity to crotyl alcohol (Fig. 6b) for the catalysts after reduction at 523 and 773 K as a function of time onstream. The monometallic Pt/TiO<sub>2</sub> catalyst shows a high selectivity in the first stages of the reaction (highest conversion values) even after reduction at low temperature. As the reaction proceeds, the conversion degree decreases due to catalyst deactivation, and the selectivity to crotyl alcohol drastically drops as well. The same behavior is followed after reduction at high temperature, although in this case, the selectivity to crotyl alcohol, taken at the same conversion degree, is higher. Furthermore, the production of hydrocarbons is similar after reduction at both temperatures, around 5%, and it is not affected by deactivation. These results indicate that active sites for the hydrogenation of the carbonyl bond are already present on the catalyst after reduction at low temperature, because the selectivity to crotyl alcohol is much higher than that obtained with platinum catalysts supported on nonreducible supports such as silica or alumina (57). However, reduction at 773 K increases the number of such sites or even creates new active sites, and the catalyst becomes more active and selective. The active sites are poisoned and/or blocked as the reaction proceeds, which causes catalyst deactivation and a drastic decrease in selectivity toward the hydrogenation of the carbonyl bond.

The evolution of the catalytic activity with time onstream at 313 K for the bimetallic PtSn/TiO<sub>2</sub> catalyst reduced at 523 and 773 K is also plotted in Fig. 5. The bimetallic catalyst is already more active than the monometallic one after reduction at low temperature, although its initial selectivity to crotyl alcohol is somewhat lower (Fig. 6b). Reduction at 773 K produces a very important increase in activity in the bimetallic catalyst, which is the opposite of the effect obtained with Pt/TiO<sub>2</sub>. It has to be taken into account that reduction at high temperature produced a strong decrease in activity for toluene hydrogenation in both catalysts, and it was related to the loss of surface platinum atoms by surface coverage with partially reduced titania. In the case of

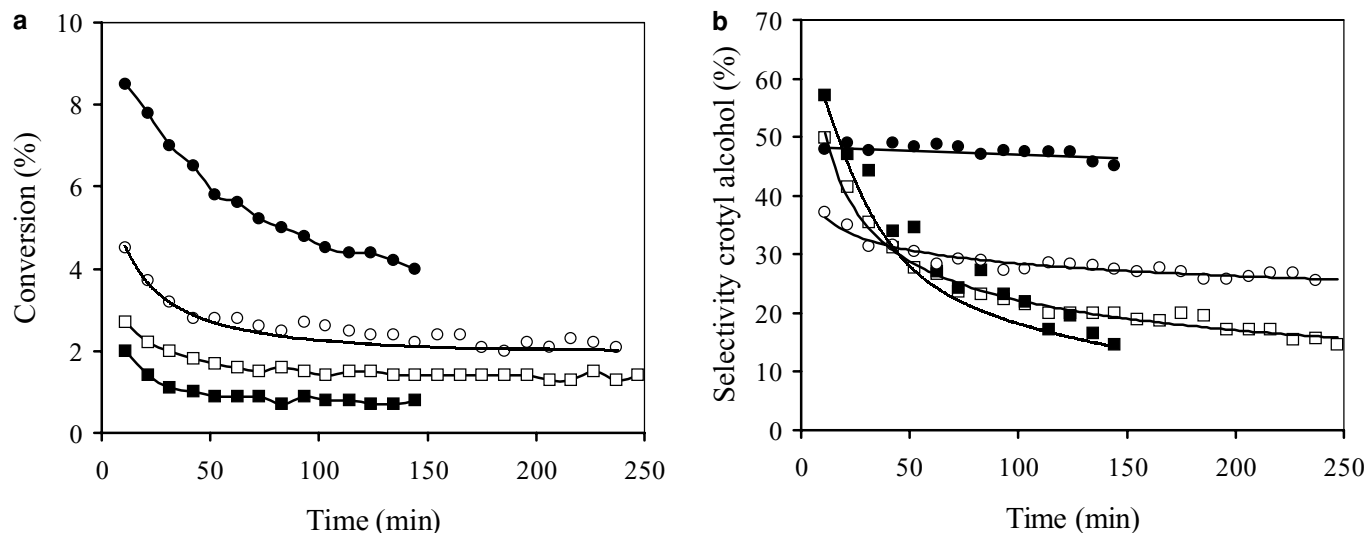


FIG. 6. Evolution of overall (a) conversion and (b) selectivity toward crotyl alcohol as a function of time onstream at 313 K for catalysts Pt/TiO<sub>2</sub> (■, □) and PtSn/TiO<sub>2</sub> (●, ○) after reduction at 523 K (open symbols) and 773 K (full symbols).

crotonaldehyde hydrogenation, the remaining platinum atoms are much more active thanks to the interfacial sites created upon reduction. It can be inferred from these results that these sites are much more active in the case of the bimetallic catalyst. The evolution of the selectivity to crotyl alcohol of the bimetallic catalyst (after reduction at 773 K) with time onstream is also different than that obtained with the monometallic catalyst. It remains practically unchanged at about 50% while the catalyst deactivates and the conversion degree decreases from 9 to 4%. It is also noteworthy that hydrocarbon production was nearly nil on this catalyst reduced at both high and low temperature.

Figure 7 summarizes the distinctive behavior of the catalysts in toluene hydrogenation and crotonaldehyde hydrogenation. It plots the ratio between the initial catalytic activity for crotonaldehyde hydrogenation (taken after 10 min onstream, when the mass balance has been achieved) and that for toluene hydrogenation on both catalysts after reduction at low and high temperatures. It can clearly be seen

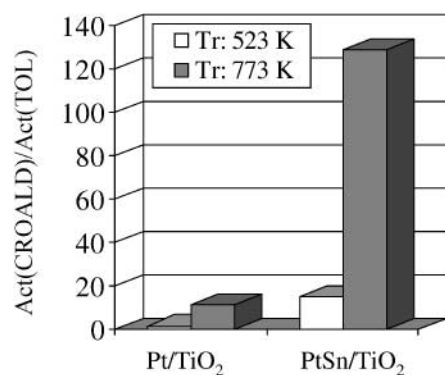


FIG. 7. Activity ratio for crotonaldehyde hydrogenation and toluene hydrogenation for catalysts reduced at 523 and 773 K.

that the presence of tin has a positive effect on crotonaldehyde hydrogenation compared to toluene hydrogenation, even after reduction at low temperature. Similarly, reduction at high temperature also favors the hydrogenation of the aldehyde. However, this effect of reduction temperature is much more important by far in the bimetallic catalyst.

It was already mentioned in the introduction section that the role of tin as a platinum catalyst promoter for the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes has been clearly stated. In these bimetallic PtSn systems, the positive effect of tin is mainly related to the presence of oxidized tin species which, acting as Lewis acids, interact with the oxygen atom of the carbonyl bond, thus weakening the bond and favoring its hydrogenation. The need for the formation of a PtSn alloy for improving the catalytic activity and selectivity has also been addressed in a recent paper dealing with Pt/SnO<sub>2</sub> catalysts prepared with different metal precursors (58). However, it has also been shown that selectivity towards crotyl alcohol is not improved at all when the reaction is carried out on model Sn/Pt(111) alloys compared to the pure Pt(111) surface, although the catalytic activity is increased up to twofold (59).

With regard to the titania-supported catalysts reported in this work, XPS analysis has shown that tin is mainly in an oxidized state after reduction at 523 K, and that the reduction treatment at high temperature only slightly increases the amount of metallic tin. The surface composition of the bimetallic catalyst after reduction at low and high temperature is therefore very similar, where the main difference detected by XPS is a certain surface enrichment with tin. But it is also necessary to take into account the decoration of the metal particles by patches of TiO<sub>2-x</sub> species taking place upon reduction at high temperature (SMSI effect). If these patches are not thick enough, the platinum surface

will be equally accessible to X rays during the XPS analysis, although some platinum atoms will be effectively covered. In this case, the Pt/Ti XPS atomic ratio would not be an actual estimation of platinum dispersion in catalysts reduced at high temperature, and it would then be lower than in the catalysts reduced at 523 K. This can explain the decrease in the catalytic activity for toluene hydrogenation when the catalysts are reduced at high temperature. The situation is completely different when the catalysts are used for crotonaldehyde hydrogenation. In this case, reduction at high temperature involves, besides the decoration of metal particles by partially reduced titania, the formation of sites at the metal–partially reduced titania support interface that are effective for activation of the carbonyl bond. These two effects are opposite, because the first one causes a lower amount of surface platinum atoms and, therefore, a lower catalytic activity, whereas the second one favors both the catalytic activity and the selectivity toward hydrogenation of the carbonyl bond. As a result, catalyst Pt/TiO<sub>2</sub> reduced at 773 K is less active than after reduction at 523 K (the first effect is more important here), but it is more selective toward the production of crotyl alcohol. The second factor is far more important in the bimetallic PtSn catalyst, leading to a much higher catalytic activity and a high selectivity, which is more stable with time onstream. The origin of this enhancement cannot be assessed from the results reported here, although a tentative explanation may simply be that an additive effect of platinum promotion occurs by oxidized tin species and by partially reduced titania. In any case, the stability of oxidized tin toward reduction is remarkable, such that only a small fraction of tin (22%) is in the metallic state after reduction at high temperature. This may be one of the factors determining the high activity and selectivity of the bimetallic PtSn/TiO<sub>2</sub> catalyst reduced at 773 K.

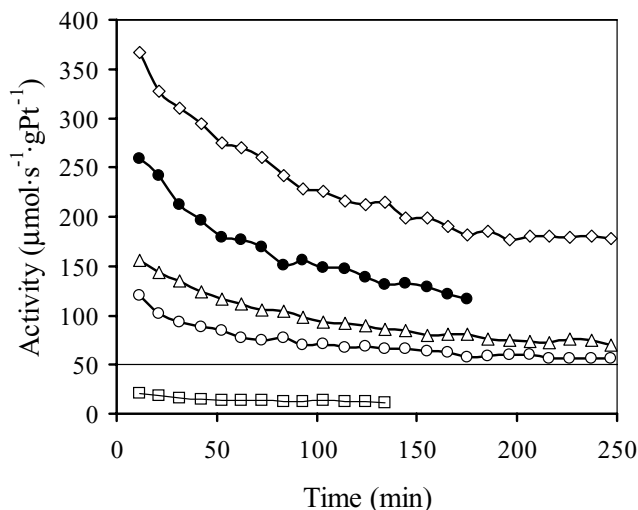


FIG. 8. Evolution of catalytic activity with time onstream at 313 K of catalyst PtSn/TiO<sub>2</sub> reduced at different temperatures: (○) 523, (●) 773, (◇) 873, (△) 973, and (□) 1073 K.

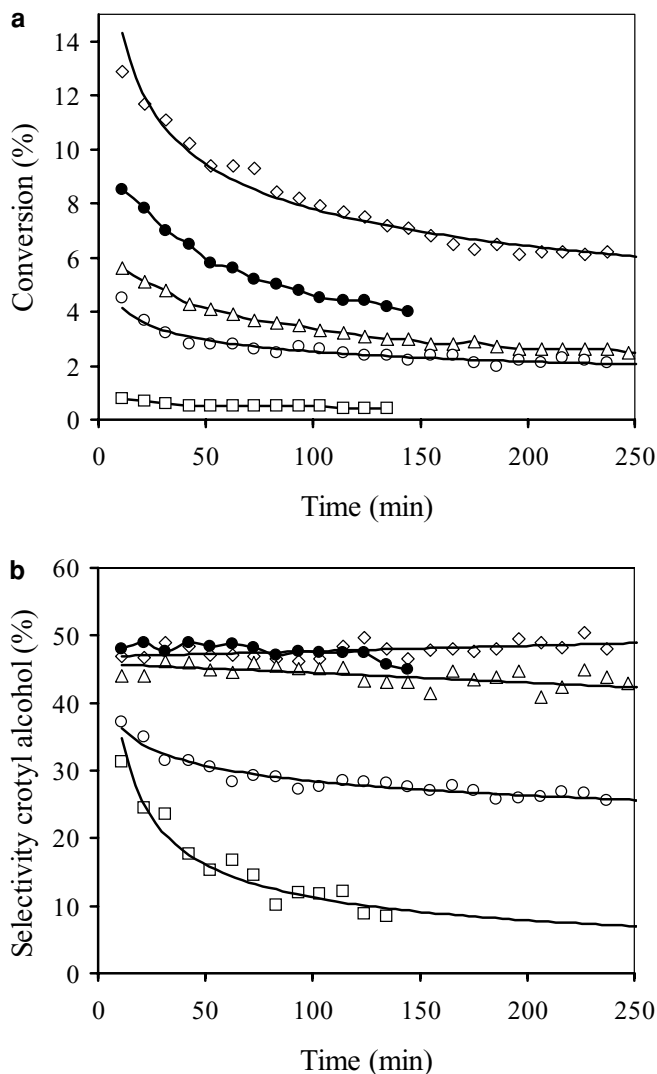


FIG. 9. Evolution of overall (a) conversion and (b) selectivity toward crotyl alcohol as a function of time onstream at 313 K for catalyst PtSn/TiO<sub>2</sub> reduced at different temperatures: (○) 523, (●) 773, (◇) 873, (△) 973, and (□) 1073 K.

In view of the great effect of the reduction temperature on the catalytic behavior of the bimetallic PtSn/TiO<sub>2</sub> catalyst in the vapor-phase hydrogenation of crotonaldehyde, the reaction has also been performed at 313 K for catalyst reduced at 873, 973, and 1073 K. The evolution of catalytic activity ( $\mu\text{mol s}^{-1} \text{gPt}^{-1}$ ) with time onstream has been plotted in Fig. 8. It can be clearly seen that the catalytic activity increases with the reduction temperature from 523 to 873 K, which seems to be the optimal reduction temperature for this system. For higher reduction temperatures the catalytic activity decreases, and the catalyst becomes nearly inactive after reduction at 1073 K.

On the other hand, Fig. 9 shows a comparison of the evolution of the overall conversion (Fig. 9a) and of the



selectivity to crotyl alcohol (Fig. 9b) for the catalyst reduced at different temperatures as a function of time onstream. Deactivation does not modify the selectivity for catalysts reduced at 773 or 873 K, which remains around 50% for conversion degrees ranging from 4 to 13%. The initial selectivity of the catalyst reduced at 973 K is also close to 50%, but it slightly decreases with time onstream as the conversion degree drops from 5 to 2%. Finally, the worst result is obtained after reduction at 1073 K. These results confirm that 873 K is the optimal reduction temperature for this catalyst, such that maximum activity is achieved while selectivity to crotyl alcohol remains at relatively high levels (close to 50%) during the experimental run.

### CONCLUSIONS

The work reported in this paper compares the catalytic behavior of Pt/TiO<sub>2</sub> and PtSn/TiO<sub>2</sub> catalysts, after low (523 K) and high (773 K) reduction temperature, in the vapor-phase hydrogenations of toluene and crotonaldehyde. XPS analysis of the catalysts reduced *in situ* has shown that in the bimetallic catalyst, tin is mainly in an oxidized state even after reduction at 773 K. The presence of tin and the reduction at high temperature have detrimental effects on catalytic activity for toluene hydrogenation. For the monometallic Pt/TiO<sub>2</sub> catalyst, reduction at high temperature causes a decrease in activity for crotonaldehyde hydrogenation, although the selectivity toward hydrogenation of the carbonyl bond is somewhat enhanced. The effect of reduction temperature is much higher in the bimetallic catalyst. In this case, reduction at 773 K produces a drastic increase in catalytic activity for crotonaldehyde hydrogenation, as well as a stable selectivity toward the unsaturated alcohol (around 50% at 4–9% conversion). Furthermore, it has been observed that 873 K is the optimal reduction temperature for this bimetallic system. Reduction at higher temperatures causes a loss in catalytic activity and selectivity to crotyl alcohol. The joint effect of oxidized tin species, which are specially stabilized by the support, and partially reduced titania is assumed to be the main origin of this behavior.

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