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Influence of Zn on the characteristics and catalytic behavior of TiO₂-supported Pt catalysts

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Abstract

Vapor-phase hydrogenation of toluene and selective hydrogenation of crotonaldehyde have been performed over Pt/TiO_2 and $PtZn/TiO_2$ after low (473 K) and high (773 K) temperature reduction. The catalysts were characterized by H_2 chemisorption, X-ray photoelectron spectroscopy (XPS), and Auger spectroscopy (AES) after each reduction treatment. Infrared spectra of CO alone and followed by the introduction of crotonaldehyde have been recorded for both catalysts after reduction at 473, 673, and 773 K. The presence of zinc and an increase in the reduction temperature strongly decreased the catalytic activity for toluene hydrogenation, but a different effect was observed for crotonaldehyde hydrogenation. After reduction at low temperature, the bimetallic catalyst was somewhat less active than the monometallic catalyst, but the initial activity of the former was greatly increased after reduction at 773 K, whereas the Pt/TiO_2 catalyst reduced at this high temperature was almost inactive. The selectivity toward the hydrogenation of the carbonyl bond exhibited a strong dependence on the presence of zinc and on the reduction temperature. Monometallic Pt/TiO_2 reduced at low temperature showed the maximum selectivity (up to 75%), although with a continuous decrease with time on stream. The bimetallic $PtZn/TiO_2$ catalyst, reduced at 773 K, showed a more stable selectivity to crotyl alcohol, centered at about 30%.

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1. Introduction

Schawb and Schultes first reported that the catalytic behavior of a supported metal could be modified by the support [1]. Later on, in the late seventies, Tauster et al. introduced the term "strong metal–support interaction" (SMSI) to label the modification of the adsorption ability of metals from groups 8, 9, and 10, supported on partially reducible oxides such as TiO₂, after reduction at high temperature (about 773 K) [2,3]. Thus, under SMSI conditions, the chemisorption ability for H₂ and CO is drastically diminished, as well as the catalytic activity for hydrogenation reactions involving olefinic C=C bonds, such as benzene hydrogenation. However, there is another group of hydrogenation reactions for which the strong metal–support interaction has been shown to be beneficial. Vannice and co-workers [4,5] showed that the activity for CO hydrogenation was much

* Corresponding author. *E-mail address:* asepul@ua.es (A. Sepúlveda-Escribano). greater on Pd/TiO2 in the SMSI state than for palladium supported on silica, alumina, or silica-alumina, and that it was also valid for Pt/TiO2. Similar results, i.e., enhanced specific activities, have been found during hydrogenation of acetone [6], crotonaldehyde [7–9], acetophenone [10], phenylacetaldehyde [11], and benzaldehyde [12] on Pt/TiO₂ catalysts. The different behavior of these systems toward the hydrogenation of the C=C and the C=O bonds gives rise to an increased chemoselectivity in reactions where molecules containing both unsaturated functional groups (crotonaldehyde, citral, cinnamaldehyde, etc.) are to be hydrogenated. In these cases, the selectivity toward the product in which the carbonyl bond has been selectively hydrogenated is increased, enabling the synthesis of industrially important unsaturated alcohols in high yield, which are important intermediates for the production of fragrances and pharmaceuticals [13]. The model proposed to explain this behavior includes the formation of special sites at the interface between the metal and the support. It is envisaged that these sites consist of partially reduced TiO_x species (or oxygen

vacancies) that could interact with the oxygen atom of the carbonyl group. In this way, the C=O bond would become weaker, thus facilitating its hydrogenation [14].

The catalytic behavior of Pt/TiO₂ and PtSn/TiO₂ catalysts was recently compared [15] in the vapor-phase hydrogenation of crotonaldehyde after reduction treatments at low (523 K) and high (773 K) temperature. The effect of the reduction temperature on the catalytic behavior was much more important for the bimetallic catalyst, such that catalytic activity strongly increased after high temperature reduction and a stable selectivity toward the unsaturated alcohol (ca. 50% at 4–9% conversion) was obtained. PtSn catalysts have been widely studied in the selective hydrogenation of carbonyl bonds to produce unsaturated alcohols [16-25]. The beneficial effect of tin has been attributed to the promoter effect of oxidized tin species, close to the platinum particles, acting as Lewis acid centers. The interaction of these sites with the oxygen atom of the carbonyl bond (a Lewis base center) weakens the C=O bond, thus facilitating hydrogenation. When titania is used as support, the combined effect of oxidized tin species and partially reduced titania was assumed to be the origin of the improved catalytic behavior of PtSn/TiO₂ reduced at a high temperature [15].

The addition of zinc to platinum also yields catalysts that are more active and selective in the hydrogenation of unsaturated aldehydes [26,27]. Furthermore, when ceria was used as support for bimetallic PtZn catalysts, the effect of reduction temperature on the catalytic activity and selectivity was similar to when bimetallic PtSn catalysts were supported on titania [28,29]. Both supports are very different in many aspects, but they are partially reducible oxides that are able to strongly interact with supported platinum after reduction at ca. 773 K.

The aim of the current work is to compare titaniasupported bimetallic PtZn with monometallic Pt catalysts subjected to both low (473 K) and high (773 K) reduction temperatures in the vapor-phase hydrogenation of crotonaldehyde.

2. Experimental

Degussa P25 with a surface area of 50 m² g⁻¹ (N₂, 77 K, BET method) was used as support after calcination at 773 K. The Pt/TiO₂ catalyst was prepared by impregnation with an aqueous solution of H₂PtCl₆·6H₂O (Johnson Matthey) to load 1 wt% Pt. After 24 h, the excess solvent was removed by flowing N₂ through the solution heated at 333 K. The PtZn/TiO₂ catalyst was prepared by coimpregnation, with an aqueous solution containing H₂PtCl₆·6H₂O and zinc nitrate to load 1 wt% Pt and 0.6 wt% Zn, and following the same procedure as for the monometallic sample. Both catalysts were dried overnight at 383 K and then calcined in air for 4 h at 673 K. The Pt content in both catalysts (ICP) was 0.7 wt%, and the zinc content was 0.4 wt%. For the later, the atomic Zn/Pt bulk ratio was 1.7.

IR experiments were carried out using a quartz cell fitted with CaF₂ windows and an external furnace. Catalysts samples were prepared as 16 mm diameter self-supporting disks by pressing 30 mg of loose powder between polished steel disks at 20 MN m⁻². Prior to measurements, samples were reduced in situ under a hydrogen flow $(50 \text{ cm}^3 \text{ min}^{-1})$ at 473, 623, or 773 K for 1 h. After the reduction treatment, samples were outgassed at the reduction temperature for 20 min to a final pressure of $\approx 10^{-5}$ Torr before cooling to ambient temperature. Pulses of CO and crotonaldehyde were introduced at 298 K using calibrated volumes and an Edwards active strain gauge to measure the size of the pulse. IR spectra were recorded at 4 cm⁻¹ resolution and averaging 100 scans per spectrum. Crotonaldehyde was purified by repeated distillations under reduced pressure. For the coadsorption measurements, 25 Torr doses of CO were initially introduced followed by evacuation at 298 K for 20 min prior to exposure to a crotonaldehyde pulse corresponding to low $(2.8 \,\mu\text{mol}\,g_{cat}^{-1})$ and high $(41.5 \,\mu\text{mol}\,g_{cat}^{-1})$ coverage of the surface.

XPS spectra were acquired with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg-K_{α} ($h\nu = 1253.6$ 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 pretreatment chamber and reduced in H₂ 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 ca. 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 TiO₂ at 458.5 eV, which provided values with an accuracy of ± 0.2 eV. The surface Pt/Ti, Cl/Ti, and Zn/Pt atomic ratios were estimated from the integrated intensities corrected for atomic sensitivity factors [30].

The vapor-phase hydrogenation of toluene and crotonaldehyde (2-butenal) was tested in a microflow reactor at atmospheric pressure and differential conditions. The catalysts (between 0.05 and 0.15 g) were reduced in situ at 473 or 773 K under flowing H₂ (50 cm³ min⁻¹) for 10 h and then cooled under H₂ to the reaction temperature. Toluene hydrogenation at 333 K was studied in a H₂/C₇H₈ ratio of 36. Crotonaldehyde hydrogenation was carried out at 333 K, using a reaction mixture (total flow: 50 cm³ min⁻¹; H₂/aldehyde ratio of 26) containing purified H₂ and crotonaldehyde (Fluka, >99.5%), which was prepared by passing H₂ through a thermostabilized 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. Chemisorption of H_2

Table 1 reports the results of H₂ chemisorption experiments on the monometallic and bimetallic samples, reduced at a low (473 K) and a high (773 K) temperature. The high hydrogen uptake of the monometallic Pt/TiO₂ catalyst after reduction at 473 K reflects a high platinum dispersion, corresponding to an average particle size of 1.4 nm, assuming a spherical particle geometry and that the average area occupied by one surface platinum atom was 0.084 nm² [31]. However, the chemisorption values drastically decreased after reduction at 773 K, reflecting a loss in the number of surface sites, suggesting either the development of a SMSI state or sintering of the metal particles. The bimetallic catalyst showed a lower chemisorption capacity than its monometallic counterpart after reduction at 473 K. At first sight, and assuming that the SMSI state has not yet been induced at this low reduction temperature, the origin of this lower ability for hydrogen chemisorption must be attributed to a poorer dispersion, possibly as a consequence of the presence of zinc. When the reduction was carried out at 773 K, the amount of hydrogen chemisorbed was nearly nil. In conclusion, the chemisorption ability of both catalysts was drastically decreased after reduction at high temperature, although the effect was much more significant for the bimetallic catalyst.

3.2. XPS characterization

The binding energies (BE) of the Pt $4f_{7/2}$ and Zn $2p_{3/2}$ levels for catalysts, both unreduced (vacuum treatment at room temperature in situ) and reduced in situ (H₂, 473 or 773 K, 1 h) are reported in Table 2 after referencing to the Ti $2p_{3/2}$ BE of 458.5 eV. In some cases two values are given, which correspond to the deconvolution of the main

Table 1 Hydrogen uptakes at room temperature obtained by chemisorption measurements

Catalyst	$T_{\rm Red}$ (K)	$H_2 \ (\mu mol \ g_{cat}^{-1})$	H/Pt (%)	
Pt/TiO ₂	473	14.2	79.1	
-	773	0.12	0.7	
PtZn/TiO ₂	473	8.04	44.9	
	773	0.01	0.06	

Table 2

XPS characterization of titania-supported Pt and PtZn catalysts

peak into two components; where appropriate, the percentage (%) contribution of each component to the main peak is reported in bracket. Table 2 also presents the Pt/Ti XPS atomic ratios for the catalysts after the different treatments. These values can be considered as an estimation of the platinum dispersion on the titania support although, for this kind of multicomponent systems, it is necessary to bear in mind that the XPS analysis can supply information from 2 to 3 nm in depth, and may therefore detect species covered by a thin film of other species. Furthermore, the Pt/Zn atomic ratios for the bimetallic catalysts and the Cl/Ti XPS atomic ratios of the two catalysts following the different reduction treatments are also reported.

The Pt 4f spectra for the unreduced and reduced catalysts are compared in Figs. 1a (Pt/TiO₂) and 1b (PtZn/TiO₂). For the unreduced (calcined after preparation) catalysts, the XPS spectra can be deconvoluted into four peaks, two of which (those placed at lower BE) correspond to the Pt $4f_{7/2}$ level and the others to the Pt $4f_{5/2}$ level. In both catalysts, the peaks arising from the Pt 4f7/2 levels are centered at 72.2 and 74.2 eV, which are assigned to partially oxidized platinum species. The exact assignation of these peaks is not easy, because the BE of core electrons are affected not only by the metal oxidation state and particle size, but also by the ligand atoms to which they are coordinated. In the case under study, two potential ligand atoms with different electronegativities, oxygen and chlorine, are available. The binding energy for platinum in a given oxidation state will be higher if it is bonded to chloride. In fact, the binding energy of the Pt $4f_{7/2}$ level for Pt(IV) coordinated to six chlorine atoms (as in the H₂PtCl₆ precursor compound) is about 75.3 eV (for K₂PtCl₆), but it decreases to 74.8 eV for PtO₂ and to 74.2 eV for Pt(OH)₄. The Pt $4f_{7/2}$ level for PtCl₂ is about 73.4 eV, whereas that for $Pt(OH)_2$ is about 72.4 eV [30].

After reduction at 473 and 773 K a single peak appeared in the range 70.4 to 70.9 eV, due to metallic platinum. The BE of Pt in the bimetallic catalyst were slightly lower (by 0.2–0.3 eV) than in Pt/TiO₂. Considering the higher Cl content in the bimetallic sample, the opposite trend would be expected if chloride were coordinated to Pt. It can be assumed that Cl is located on the titania, and that the small differences in binding energies are due to Zn. The relative amounts of surface Pt (Pt/Ti XPS atomic ratio) strongly decreased with reduction, although no difference was apparent between 473 and 773 K reduced samples, confirming that

Catalyst	Treatment	Pt 4f _{7/2} BE (eV)	Pt/Ti	Pt/Zn	Cl/Ti	Zn 2p _{3/2} BE (eV)
Pt/TiO ₂	_	72.2 (36.8) 74.3 (63.2)	0.020	_	0.029	_
	Reduced 473 K	70.9	0.011	-	0.014	_
	Reduced 773 K	70.7	0.013	_	0.007	-
PtZn/TiO ₂	-	72.2 (39.2) 74.1 (60.8)	0.024	0.55	0.065	1022.2
	Reduced 473 K	70.7	0.013	0.34	0.032	1022.0
	Reduced 773 K	70.4	0.013	0.16	0.015	1021.9



Fig. 1. XPS Pt 4f spectra of the unreduced and reduced catalysts: (a) Pt/TiO_2 ; (b) $PtZn/TiO_2$.

loss in H_2 uptake after reduction at high temperature (Table 1) was a consequence of SMSI rather than sintering.

The possibility of Pt–Zn bimetallic particle formation, confirmed by XRD analysis, has been reported for this kind of system, including PtZn alloy formation after 473 K reduction of a Pt/ZnO catalyst, prepared from H_2PtCl_6 [26]. The choice of precursor seems to be very important, as a higher reduction temperature was required when [Pt(NH₃)₄](NO₃)₂ was used [26]. Formation of a Pt₃Zn alloy after 573 K reduc-



Fig. 2. Zn LMM Auger spectra of the bimetallic PtZn/TiO₂ catalyst.

tion was reported for a $Pt/ZnAl_2O_4$ catalyst, prepared from H_2PtCl_6 , and a PtZn alloy when the reduction was carried out at 773 K [32].

XRD analysis here did not allow features other than those corresponding to the titania to be distinguished due to the low metal content employed. Furthermore, XPS analysis does not permit reliable verification of the formation of Pt-Zn alloy phases in these catalysts. The BE of the Pt $4f_{7/2}$ level was similar for both the Zn-free and the Zn-containing catalyst after reduction treatments at low and high temperatures. The BE of the Zn 2p3/2 transition for the fresh bimetallic catalyst presents a single band centered at 1022.2 eV, which can be unambiguously assigned to Zn(II) species. Reduction at 473 K produced a small shift to 1022.0 eV, while reduction at high temperature (773 K) shifted it further to 1021.9 eV. The difficulty of assessing the zinc oxidation state by XPS is well recognized, owing to the similarity in binding energies of metallic zinc and Zn(II); however, the Zn LMM Auger transition is more sensitive [33]. In any case, it must be remarked that the presence of metallic zinc does not directly imply the formation of alloy phases. Fig. 2 shows the Zn LMM Auger spectra obtained for the fresh catalyst and for the catalyst reduced at 473 and 773 K. A zinc foil gave a spectrum that showed two well-defined bands centered at kinetic energies of 993 and 988 eV, due to metallic and oxidized zinc species, respectively. The spectrum obtained with the fresh sample shows a main band centered at 988.1 eV, which indicates the presence of Zn(II) species in this catalyst, as well as a lower intensity band at 991.1 eV. This later can be tentatively assigned to metallic Zn, although in an electron-deficient state. Reduction at 473 K increased the contribution at higher kinetic energy, which could indicate reduction of zinc. Reduction at high temperature produced a



Fig. 3. Infrared spectra of a Pt/TiO_2 catalyst reduced at (A) 473 K, (B) 623 K, and (C) 773 K and exposed to (—) 0.1 Torr CO, (…) 0.5 Torr CO, (–––) 25 Torr CO and then outgassed at 298 K for (–…–) 30 s and for (–…) 40 min.

broad band that could be formed by two contributions, one of them centered at 991 eV and the other at 989 eV. In conclusion, results suggest the progressive reduction of Zn(II) by increasing the reduction temperature, such that about 50% was in the metallic state after 773 K.

Increasing the reduction temperature from 473 to 773 K had no effect on the relative amount of surface platinum in either catalyst, as indicated by the Pt/Ti XPS atomic ratios (Table 2). For the bimetallic catalyst, the Pt/Zn XPS atomic ratio decreased sharply (from 0.55 to 0.16) with increased reduction temperature. It is expected that metallic zinc would be in the liquid state at 773 K (melting point: 693 K), and that it would readily spread over the support giving rise to increased amounts detected by the XPS measurements. Despite the high mobility of Zn atoms under these conditions, the similarity in Pt/Ti XPS ratios for catalyst reduced at either temperature would suggest that platinum was not diluted nor covered by zinc atoms, unless the latter were present as a very thin layer that allowed the X-ray-induced electrons emitted from the underlying platinum atoms to be detected. A similar conclusion may be drawn regarding the titania support even though it is expected that upon 773 K reduction, titanium suboxide patches may be formed with the potential to migrate from the support and decorate the surface of platinum crystallites. The similarity in the Pt/Ti XPS atomic ratios observed after reduction at both low and high temperatures indicates that, at most, only very thin patches of TiO_{2-x} might cover the metal particles.

3.3. Adsorption of CO on reduced Pt/TiO₂ and PtZn/TiO₂ catalysts

Spectra at low coverage (0.1 Torr) of CO on Pt/TiO_2 reduced at 473 K (Fig. 3A) exhibited peaks at 2088 and



Fig. 4. Infrared spectra of a PtZn/TiO₂ catalyst reduced at (A) 473 K, (B) 623 K, and (C) 773 K and exposed to (—) 0.1 Torr CO, (…) 0.5 Torr, (---) 25 Torr CO and then outgassed at 298 K for (---) 30 s and for (---) 40 min.

 2076 cm^{-1} and a low frequency shoulder on the main band, together with a low intensity peak at 1849 cm⁻¹ due to bridge-bound CO. An increase in the CO pressure produced a blue shift of the main bands to 2092 and 2082 cm⁻¹, as well as the reversal of their relative intensities. A band centered at 2186 cm⁻¹ was also discerned which is associated with CO adsorbed at exposed Ti cation sites of the support. Finally, after 40 min evacuation, the only features observed were the two main bands, centered at 2088 and 2076 cm⁻¹, and shoulders at ca. 2060 and 2040 cm⁻¹.

IR spectra of CO adsorbed at low coverages (0.1 Torr) on Pt/TiO₂ reduced at 623 K (Fig. 3B) showed the same features as those obtained after reduction at 473 K, although the features were shifted to slightly lower frequencies. An increase in the CO pressure caused an increase in the relative intensity of the low frequency band such that only a broad band, centered at 2086 cm⁻¹ was observed after introduction of 25 Torr of CO. Evacuation removed part of the adsorbed CO to reveal the position of both bands, the lower frequency component at 2076 cm⁻¹ remaining with a higher relative intensity than observed for the 473 K reduced surface. Bridge bound CO (1849 cm⁻¹) was less prominent for the 673 K reduced sample than after reduction at 473 K.

Consistent with results of hydrogen chemisorption (Table 1), the ability of the catalyst to adsorb CO was drastically decreased after reduction at 773 K (Fig. 3C). A very low intensity band at 2080 cm⁻¹ was observed after introducing the highest CO pressure, and this was shifted to 2072 cm⁻¹ following evacuation. Evidence for CO on bridging sites was not observed.

Fig. 4 shows IR spectra for CO adsorbed on the $PtZn/TiO_2$ catalyst after low (A: 473 K), intermediate (B: 623 K), and high (C: 773 K) temperature reduction. All spectra exhibit bands in the 2100–2050 cm⁻¹ region due to CO linearly adsorbed on the different metallic sites. After 473 K re-

duction and exposure to a low pressure (0.1 Torr) of CO, spectra show a broad band centered at 2080 cm⁻¹, which was blue-shifted and increased in intensity with increased CO pressure. The band was composed of two or more unresolved contributions, the relative intensity of the highest frequency component being enhanced to a greater extent by an increase in CO pressure. After evacuation, an asymmetrical band at 2085 cm⁻¹ with a significant tail toward low frequencies was obtained. A very weak maximum at 1855 cm⁻¹ due to bridge-bound CO was also detected.

The spectra obtained after the introduction of 0.1 Torr of CO to the bimetallic catalyst reduced at 673 K showed a low intensity band centered at 2070 cm⁻¹. However, an intense and relatively sharp band centered at 2079 cm⁻¹ was obtained after introducing a higher CO pressure (0.5 Torr) and this was further blue-shifted at higher CO pressures. The initial band position (2080 cm⁻¹) was restored after evacuation. As in the case of the Pt/TiO₂ catalyst, 773 K reduction drastically decreased the intensity of the bands of adsorbed CO, although the effect was much greater in this case. The loss of CO adsorption capacity correlates well with the hydrogen chemisorption data, which showed that the suppression of the chemisorption ability as a result of the reduction treatment at 773 K was more significant for the PtZn catalyst.

Spectra of adsorbed CO [34] show important differences depending on the presence or absence of zinc. The spectra corresponding to the Pt/TiO2 catalyst reduced at 473 and 623 K exhibit a resolved component at 2088 cm^{-1} , a band at 2076 cm^{-1} , which was the most intense after evacuation, and a tail between 2060 and 2020 cm⁻¹, probably containing many distinct contributions. A previous study of Pt/TiO2 showed bands at 2094 and 2084 cm^{-1} [35], with the former attributed to CO adsorbed on (111)-type facets, where the carbonyls experience the greatest number of dipole coupling interactions. A band at 2084 cm⁻¹ was associated with terrace sites which were less extended or where the metal atoms were in a less dense close packing arrangement. In the present study, the two bands appear at somewhat lower frequencies (2088 and 2076 cm^{-1}). Assuming that these frequencies are a consequence of the coordination number on the adsorbent Pt atom and the dipole-dipole interactions with neighboring adsorbed CO molecules, results would indicate that the crystallites were composed of rough surfaces with short terrace length and a high proportion of low coordination sites.

Reduction at 773 K produced a dramatic decrease in IR band intensity, which correlates with the loss of hydrogen chemisorption. This is not due to platinum sintering, as larger particles would display a greater proportion of high frequency carbonyls due to the abundance of close packed faces, and one would expect a reduction in the Pt/Ti XPS atomic ratios, which remain constant over this temperature range (Table 2). It has been argued [35] that suboxides of titanium have a preference for the densest packed platinum faces, such that a loss of intensity of the high frequency component may accompany decoration of the Pt surface.

Spectra of PtZn/TiO₂ catalysts show important differences to those of Pt/TiO₂, even after reduction at 473 K. Although the bandwidth may indicate the presence of two contributions, these were not resolved. The intensity of the bands obtained after 0.1 Torr of CO was much lower than for Pt/TiO₂, possibly suggesting a lower initial adsorption enthalpy for CO in the presence of Zn. At higher CO pressures, the overall band intensities were comparable for PtZn/TiO₂ and Zn-free catalyst, indicating, in line with H₂ chemisorption values (Table 1), that the number of sites available for CO was similar for both catalysts.

The effects described above for catalysts reduced at 473 K were further emphasized for 623 K reduced catalysts, where the CO band at low coverage (0.1 Torr) on the bimetallic PtZn catalyst had a much lower intensity than the Zn-free catalyst. Assuming the same extinction coefficient for adsorbed CO on both catalysts, these results again suggest a lower initial adsorption enthalpy of CO in the presence of Zn. As this effect was more dramatic for 623 than 473 K reduction, this may imply an increased role of reduced Zn in modifying the platinum characteristics. The intensities of the peaks at full coverage were comparable for Zn-containing and Zn-free catalysts. An important difference in the IR spectra was the absence, for the Zn-containing catalyst, of the high frequency band at 2088 cm⁻¹ in the Zn-free sample. This may reflect a change in the particle morphology as a result of a change in the nature of the support or as a consequence of Pt-Zn interactions or involve a dilution effect of zinc atoms or ions on the CO adsorbed on the low-index facets of platinum crystallites. The dilution of a surface with atoms or ions that are unable to chemisorb CO would produce a decrease in the dipole-dipole interactions between adsorbed CO molecules. The decrease of the high frequency contribution (2091 cm⁻¹) was more important for higher reduction temperatures (Fig. 4), which could be interpreted in terms of a greater amount of mobile, metallic zinc available to dilute the platinum surface.

3.4. Coadsorption of CO and crotonaldehyde

Fig. 5 shows IR spectra corresponding to the adsorption of CO on the Pt/TiO₂ catalyst followed by evacuation and the introduction of low and high coverage doses of crotonaldehyde. Irrespective of the catalyst reduction temperature, interaction of crotonaldehyde produced a red shift in maxima of linearly and bridged-bonded CO as observed using a similar Pt/TiO₂ catalyst [35]. The sample reduced at 473 K (Fig. 5A) exhibited bands at 2092 and 2080 cm⁻¹. A low coverage crotonaldehyde pulse produced only very slight modifications, with a small decrease in intensity of the two main bands and a slight increase in intensity at ca. 2040 cm⁻¹. At higher crotonaldehyde coverage, the band at 2092 cm⁻¹ completely disappeared, while the low frequency component shifted to 2073 cm⁻¹ and its intensity some-



Fig. 5. Infrared spectra of a Pt/TiO_2 catalyst reduced at 473 K, 623 K, and 773 K, exposed to 25 Torr CO followed by outgassing at 298 K for 20 min (—) and exposure to a low coverage pulse of crotonaldehyde (…) and a high coverage crotonaldehyde pulse (…).

what decreased, and a broad band appeared with a maximum centered at 2053 cm^{-1} . The maximum due to bridge-bound carbonyls was also red-shifted by the presence of the coadsorbate.

The sample reduced at 623 K showed qualitatively similar behavior to the 473 K reduced sample. Following CO exposure and evacuation, the IR spectrum (Fig. 5B) exhibited maxima at 2092 and 2080 cm⁻¹, as well as low frequency contributions. Exposure to a low coverage pulse of crotonaldehyde produced a decrease in the intensity of the high frequency component, whereas the lower frequency band suffered a 5 shift to 2075 cm⁻¹ without significant loss of intensity. The effect was further pronounced at higher crotonaldehyde coverage, where the main band was red-shifted to 2060 cm⁻¹ and the intensities of the bands contributing to the tail at lower frequencies were increased. The band due to bridge-bound carbonyls was not observed following introduction of crotonaldehyde.

After high reduction temperature, the Pt/TiO₂ catalyst exposed to CO and evacuation exhibited a broad band of low intensity with maxima at 2089 cm⁻¹ and a tail at lower frequencies. Exposure to a low coverage crotonaldehyde pulse produced a red shift of this band to 2086 cm⁻¹, with a slight increase in intensity. Spectra after exposure to higher crotonaldehyde vapor pressure showed a high frequency component at 2092 cm⁻¹ of low intensity. The intensity of the overall band envelope increased and the maximum now appeared at 2066 cm⁻¹, with the tail that appeared in catalysts reduced at lower temperatures still present.

Fig. 6 shows spectra obtained following the coadsorption of CO and crotonaldehyde over the $PtZn/TiO_2$ catalyst after reduction at 473 K (A), 623 K (B), and 773 K (C). As in the case of the monometallic catalyst, interaction of crotonaldehyde with a CO-covered surface produced a red shift of the overall band envelope, and the development of in-



Fig. 6. Infrared spectra of a PtZn/TiO₂ catalyst reduced at (A) 473 K, (B) 623 K, and (C) 773 K, exposed to 25 Torr CO followed by outgassing at 298 K for 20 min (—) and exposure to a low coverage pulse of croton-aldehyde (…) and a high coverage crotonaldehyde pulse (·---).

tense contributions at low frequencies (between 2060 and 1950 cm⁻¹). The catalyst reduced at 473 K and precovered with CO exhibited a broad band centered at 2085 cm^{-1} together with a shoulder at 2072 cm⁻¹ and considerable asymmetry toward lower frequencies. Exposure to crotonaldehyde produced a slight red shift of the maximum to 2084 cm⁻¹, and an increase of the intensity of the shoulder at 2072 cm^{-1} and of the contributions at lower frequencies. After exposure to higher vapor pressure of crotonaldehyde, the high frequency component was completely removed and the maximum now observed at 2076 cm^{-1} , corresponded to the shoulder appearing in the previous spectra. In addition, the intensity of the tail contributions (ca. 2040 cm^{-1}) was greatly increased. The bridge-bound carbonyl band suffered a similar fate and was displaced by ca. 10 cm^{-1} but without significant intensity loss. Similar behavior was observed for the sample after reduction at 623 K. Exposure to CO alone showed a single, symmetric peak centered at 2081 cm^{-1} , with a small contribution at about 2040 cm⁻¹. Introduction of crotonaldehyde only slightly (2 cm^{-1}) perturbed the spectrum, with no significant loss of intensity, although exposure to a high coverage pulse produced a displacement of the maximum to 2067 cm^{-1} , together with the development of contributions at ca. 2040 cm^{-1} , and also displaced the maximum due to bridge-bound carbonyls by ca. 10 cm $^{-1}$. Reduction of the PtZn/TiO2 catalyst at the highest temperature (773 K) followed by exposure to CO produced a sharp, symmetrical maximum centered at 2078 cm^{-1} . The intensity of the linear carbonyl bands observed in the sample reduced at this high temperature was very low, consistent with the low adsorption capacity of the SMSI state. No bridge-bound species were detected. Exposure to a low coverage pulse caused a slight red shift of the maximum, with a decrease in the intensity. At higher crotonaldehyde coverage, a broad



Fig. 7. Catalytic activity for toluene hydrogenation at 333 K of catalysts Pt/TiO_2 and $PtZn/TiO_2$ after reduction at low (473 K) and high (773 K) temperature.

band centered at 2058 cm^{-1} and a tail of considerable intensity reaching 1960 cm^{-1} was seen. The overall band area was more intense in the presence of the coadsorbate than for CO alone.

3.5. Toluene hydrogenation

Fig. 7 plots the activity for toluene hydrogenation (micromoles of toluene transformed per gram of platinum per second) at 333 K on both the monometallic and the bimetallic catalysts after reduction at 473 and 773 K. For the catalysts reduced at low temperature, in which the SMSI effect is not expected, the bimetallic catalyst showed a much lower activity than the monometallic catalyst on a per gram of Pt basis. Even when considering the lower Pt dispersion for the Zncontaining catalysts (Table 1), the activity was still low with respect to the Zn-free sample. Toluene hydrogenation is considered a structure-insensitive reaction, and the catalytic activity should only depend on the number of surface platinum atoms and not on the metal particle size or morphology. The lower catalytic activity of the PtZn/TiO2 catalyst compared with the Zn-free sample should be directly related to the relative amount of platinum surface atoms for both catalysts. XPS showed a surface Pt/Ti atomic ratio, which was similar for both catalysts reduced at 473 K (0.011 for Pt/TiO₂ and 0.013 for PtZn/TiO₂). However, chemisorption resulted in very different H/Pt ratios: 0.79 for Pt/TiO2 and 0.45 for PtZn/TiO₂. Assuming a H:Pt_s stoichiometry of 1:1, these values for dispersion (Table 1), together with those for catalytic activity (Fig. 7), indicate specific activity (TOF) values of 218 h^{-1} for Pt/TiO₂ and 78 h^{-1} for PtZn/TiO₂ for these catalysts in toluene hydrogenation at 333 K. Even allowing for the lower number of surface Pt atoms in the bimetallic catalysts (as shown by chemisorption measurements), the specific activity (per surface platinum atom) was decreased in the presence of zinc.

The decrease in specific activity of noble metal catalysts in structure-insensitive reactions when a second nonactive metal is added has been reported, although the origin has not been clearly elucidated. Electronic effects of germanium on Pt have recently been invoked to explain the decrease in activity in toluene hydrogenation of bimetallic Rh-Ge catalysts as the amount of germanium was increased [36]. Alexeev et al. obtained lower hydrogen chemisorption and toluene hydrogenation activity for alumina-supported Pt-W catalysts reduced at 673 K [37]. They argued that both the lower ability for chemisorbing hydrogen and the increased electron density on Pt as a result of bimetallic interactions could account for the modified catalytic behavior of their samples. Thus, a low hydrogen surface concentration could account for the low rate of the rate-determining step (the addition of the first hydrogen atom to the aromatic ring [38]), and a high electron density on platinum would hinder the otherwise fast step of toluene chemisorption on platinum. However, Chandler et al. discarded the electronic effects as the origin of the decrease in hydrogen chemisorption and catalytic activity for toluene hydrogenation [39], as the electronic effect of alloy formation would involve the electron enrichment of platinum and, therefore, the enhancement of its ability to bind and dissociate hydrogen. These authors proposed that both particle size effects and ensemble effects could account for the reduced hydrogen binding and lower toluene hydrogenation activity of the bimetallic catalysts. Gates and co-workers suggest that, although toluene hydrogenation might not be considered as a structure-insensitive reaction, this for particles smaller than 1.0 nm [40]. Results for the PtZn/TiO₂ catalyst after 473 K reduction show a modification, which is unlikely to exist if at least part of the zinc had not been reduced to the metallic state.

Reduction of Pt/TiO_2 at high temperature produced a drastic decrease in the toluene hydrogenation activity, due to the strong metal–support interaction. H₂ chemisorption was also decreased by this treatment and thus, the specific activity (turnover frequency) value was significantly affected by the precision of the chemisorption measurement. Similar behavior was observed for the Zn-containing catalyst that, again, was less active than its Zn-free counterpart.

3.6. Crotonaldehyde hydrogenation

Fig. 8 plots the evolution of the overall catalytic activity (micromoles of crotonaldehyde transformed per second per gram of Pt) as a function of time on stream at 333 K for Pt/TiO₂ and PtZn/TiO₂ reduced for 10 h at 473 and 773 K. The initial data were taken after 4 min on stream, when the carbon balance was achieved. Prior to this, a proportion of reactant and products were adsorbed by the catalyst and no reliable measurements could be performed.

After an initial period of deactivation, the activity remained quite stable. The only exception was the 773 K reduced Pt/TiO₂, which showed very low activity even from the initial stages of reaction. After reduction at 473 K, Pt/TiO₂ showed an initial activity above 600 μ mol s⁻¹ g Pt⁻¹, and deactivated with time on stream to reach a steady-state activity of about 90 μ mol s⁻¹ g Pt⁻¹. Consistent with previous reports [8,9,35,41], high temperature reduction (773 K) Fig. 8. Evolution of catalytic activity for crotonaldehyde hydrogenation with time on stream at 333 K for catalysts Pt/TiO₂ (□■) and PtZn/TiO₂ (○●) after reduction at 473 K (open symbols) and 773 K (full symbols).

caused a dramatic decrease in activity, which can be attributed to the loss of surface platinum atoms due to patches of partially reduced TiO2. However, the process also involves the creation of specially active sites at the platinumsupport interface. As a result, the turnover number, i.e., the catalytic activity per surface platinum atom measured by hydrogen chemisorption, usually increases [9,35]. In this case, the initial turnover number for crotonaldehyde hydrogenation increased from 588 h^{-1} for Pt/TiO₂ reduced at 473 K, to 2120 h^{-1} after reduction at 773 K. It has been proposed that crotonaldehyde is adsorbed at these interfacial sites in such that the oxygen atom of the carbonyl bond interacts with the Lewis acid sites (coordinatively unsaturated titanium cations) of the partially reduced support. This interaction weakens the C=O bond and facilitates hydrogenation [8]. In this way, the selectivity toward crotyl alcohol through the preferential hydrogenation of the carbonyl bond is expected to increase after reduction at high temperature.

Hydrogenation of crotonaldehyde can proceed through either: (i) hydrogenation of the C=C bond to yield butanal or (ii) hydrogenation of the C=O bond to yield crotyl alcohol (2-buten-1-ol). In a second stage, butanal, and crotyl alcohol can be further hydrogenated to butanol, and crotyl alcohol may also isomerize to butanal. The overall selectivity of the process is initially defined by the ratio between the hydrogenation rates of the C=C and of the C=O bonds, although secondary reactions play their role as the conversion degree increases usually decreasing the selectivity to the desired product, crotyl alcohol [7,18,19]. Under the conditions used here, the only products detected were butanal, crotyl alcohol, and butanol, the latter only being observed during the initial stages of the reaction. Fig. 9 compares the evolution of the overall conversion (Fig. 9a) and of crotyl alcohol selectivity (Fig. 9b) for the catalysts after reduction at 473 and 773 K as a function of time on stream. For the Pt/TiO2 Fig. 9. Evolution of (a) overall conversion and (b) selectivity toward crotyl alcohol as a function of time stream at 333 K for catalysts Pt/TiO_2 ($\Box \blacksquare$) and PtZn/TiO₂ (○●) after reduction at 473 K (open symbols) and 773 K (full symbols).

catalyst reduced at 473 K there was a sudden increase in selectivity during the first minutes of reaction, reaching a maximum of 76% after 13 min on stream. From there on there was a decrease in selectivity until reaching a nearly constant value of 25%. On the other hand, the same catalyst reduced at 773 K yielded 16% crotyl alcohol during the first stages of the reaction, and then dropped to zero after only a few minutes on stream. This result is in contrast to that expected from the mechanism described above for the promoter effect of the partially reduced titania support. An increase in selectivity to crotyl alcohol would be expected or, at least, not such a significant loss in selectivity, as early deactivation processes may affect these sites in a different way. However, product determination may be affected by the low activity of this catalyst. In fact, results obtained in a recent study [15] have shown that the Pt/TiO2 catalyst reduced at



1200

1000



773 K for 4 h was somewhat less active in crotonaldehyde hydrogenation at 313 K (initial activity: 50 μ mol s⁻¹ g Pt⁻¹) than the same catalyst reduced for 4 h at 523 K (initial activity: 75 μ mol s⁻¹ g Pt⁻¹), but the selectivity toward crotyl alcohol was very similar after both reduction treatments.

The evolution of the activity at 333 K for the PtZn/TiO₂ catalyst reduced at 473 and 773 K is also plotted in Fig. 8. PtZn/TiO2 reduced at 473 K was less active than the Znfree catalyst in agreement with the lesser number of surface platinum atoms available (Table 1). The activity of the PtZn/TiO₂ strongly increased after 773 K reduction, such that an initial activity of 1100 μ mol s⁻¹ g Pt⁻¹ was reached, a value 50 times greater than that obtained with the Zn-free catalyst under similar conditions. It should be considered that reduction at 773 K caused a drastic decrease in the hydrogen chemisorption ability of this catalyst and in its catalytic activity for toluene hydrogenation, and these effects were explained on the basis of the SMSI effect by which the platinum was decorated by partially reduced titania. The high activity for crotonaldehyde hydrogenation would indicate that, despite the diminished number of surface sites after reduction at 773 K, the remainder were much more active, or that new sites, e.g., at the Pt-support interface were created which were very active. Zn has a very important role in this phenomenon, as the Zn-free catalysts strongly deactivated after reduction at 773 K. Similar results have recently been obtained in a study on the effect of reduction temperature on the properties and catalytic behavior of Pt-Sn and Pt-Zn catalysts supported on partially reducible oxides (CeO₂, TiO_2 [15,28]. The evolution of crotyl alcohol selectivity for the bimetallic catalyst reduced at both temperatures is plotted in Fig. 9b as a function of time on stream. Two different patterns are clearly observed. First, catalyst reduced at 473 K behaves as the Zn-free catalyst reduced at the same temperature, i.e., a maximum in selectivity (about 60%) after 12 min on stream, followed by a continuous decrease to values below 10%. On the other hand, the selectivity obtained with the bimetallic catalyst reduced at 773 K also increased with time on stream during the first stages of the reaction, but it stabilized at around 30%.

The increased crotyl alcohol selectivity observed during the first stages of the reaction for all catalysts, with the exception of Pt/TiO₂ reduced at 773 K, is not related to the formation of selective sites, but rather with the general deactivation. During the first minutes on stream not only butanal and crotyl alcohol are produced, but also butanol due to the consecutive hydrogenation of the two initial products. This is related to the relatively high degree of conversion achieved, and was not detected when working at conversions below 10% [15]. The amount of butanol quickly decreased, but the behavior differed depending on the catalyst and on the reduction treatment. Fig. 10 compares the selectivity toward crotyl alcohol and butanol, during the first 35 min on stream. The remaining product (to sum 100% selectivity) was butanal. For Pt/TiO₂ reduced at 473 K the initial selectivities for crotyl alcohol and butanol were very similar (around



Fig. 10. Evolution of selectivity toward butanol (open symbols) and crotyl alcohol (full symbols) as a function of time stream at 333 K for catalysts Pt/TiO₂ reduced at 473 K (\bigcirc •), PtZn/TiO₂ reduced at 473 K (\square •), and PtZn/TiO₂ reduced at 773 K (\triangle •).

32%), but no butanol was detected after 12 min. When the PtZn/TiO₂ catalyst was reduced at 473 K, butanol, which was initially produced with 25% selectivity, did not appear after only 10 min on stream. However, when this catalyst was reduced at 773 K, the initial butanol selectivity was more than 50%, whereas crotyl alcohol was produced in a very low amount. As the reaction proceeded, selectivity to butanol decreased, reaching zero after 30 min on stream, whereas crotyl alcohol selectivity increased and remained constant at about 30%.

The low amount of crotyl alcohol produced with PtZn/ TiO₂ reduced at 773 K was obtained at a conversion of about 70%, indicating the importance of secondary reactions on the selectivity at high conversion. However, the maxima in selectivity to crotyl alcohol, which coincides with the disappearance of butanol among the products, was achieved at similar conversions for the three systems: 22% for Pt/TiO₂ (473 K) and PtZn/TiO₂ (773 K), and 10% for PtZn/TiO₂ (473 K).

When Pt/TiO₂ and PtZn/TiO₂ were reduced at 473 K, when no reduction of titania is expected, the role of zinc is evident. The H₂ chemisorption ability and toluene hydrogenation activity were decreased, suggesting a reduction in surface platinum atoms compared to the monometallic catalyst, possibly due to dilution by metallic zinc or patches of zinc oxide. However, XPS analysis suggested that loss of Pt sites due to Zn coverage was not significant. Reduced activity for crotonaldehyde hydrogenation for the bimetallic catalyst and the evolution of selectivity toward crotyl alcohol were similar to those obtained with Pt/TiO₂, although the bimetallic catalyst lost its initial selectivity more quickly. However, the decrease in crotonaldehyde hydrogenation activity as a consequence of the presence of zinc was not as important as that observed in toluene hydrogenation. This implies that loss of surface Pt atoms was accompanied by formation of other active centers which promoted the hydrogenation of the unsaturated aldehyde. IR spectra of adsorbed CO (Figs. 3 and 4) reveal subtle differences between the mono and bimetallic catalysts that might be attributed to the influence of zinc even after reduction at 473 K, with the influence increasing after reducing at higher temperatures. A role of $Zn^{\delta+}$ sites at the Pt–support interface cannot be ruled out.

The high initial selectivity to crotyl alcohol for Pt/TiO_2 reduced at 473 K must be assigned to the characteristics of the platinum if it is assumed that reduction of the support had not commenced. This high selectivity has been related to the abundance of Pt(111) surfaces, which optimize configuration for crotonaldehyde adsorption via the carbonyl bond [8,42]. Surface Zn atoms would disrupt that surface geometry, modifying the adsorption mode for the crotonaldehyde. The effect would be to decrease the selectivity to crotyl alcohol, although this would be compensated by any positive effect on selectivity due to the newly formed active sites.

The reduction temperature has a strong influence on the catalytic behavior. The monometallic catalyst was almost inactive for toluene and crotonaldehyde hydrogenation after reduction at 773 K. Reduction at 773 K for 10 h caused partial reduction of the support, leaving few remaining exposed platinum centers as indicated by the hydrogen uptake and the IR of adsorbed CO. Reduction at 773 K for only 4 h yielded a Pt/TiO₂ catalyst that was still relatively active and showed a high initial selectivity toward crotyl alcohol [15]. Reduction of the PtZn/TiO₂ catalyst at 773 K for 10 h, on the other hand, produced a drastic increase in the initial activity compared to the same catalyst reduced at low temperature. In this case, the reduction treatment causes two main phenomena: first, enhanced reduction of zinc, which increased the interaction with platinum; and second, the onset of the SMSI effect [43,44]. The combined effects are the origin of the observed catalytic behavior. It also seems clear that decoration of Pt by partially reduced titania is not as extended as in the absence of zinc, although it is sufficiently important to render the catalyst inactive for toluene hydrogenation. The possibility of some interaction between the support and the zinc species which could stabilize the titania surface is being considered.

4. Conclusions

The catalytic behavior of Pt/TiO_2 and $PtZn/TiO_2$ catalysts after 473 and 773 K reduction was compared in the hydrogenation of toluene and crotonaldehyde. XPS analysis has shown only small differences between the Pt $4f_{7/2}$ binding energies in the mono- and bimetallic catalysts, as well as similar Pt/Ti atomic ratios irrespective of the reduction temperature. AES analysis of the Zn LMM region has shown that Zn(II) becomes progressively reduced as the reduction temperature is increased, thus offering the possibility of Pt–

Zn interaction. The combined effects of the presence of zinc and the high temperature reduction have detrimental effects on the catalytic activity for toluene hydrogenation. After reduction at low temperature, the bimetallic catalyst was somewhat less active in the vapor-phase hydrogenation of crotonaldehyde and also less selective toward crotyl al-cohol than Pt/TiO₂. This behavior was drastically modified after reduction at high temperature. While the monometal-lic catalyst was essentially deactivated, the initial activity of the PtZn/TiO₂ sample was greatly improved. Furthermore, its selectivity toward crotyl alcohol remains stable at about 30% during time on stream, despite the strong deactivation during the first hour of reaction. The combined effects of the partially reduced titania and the presence of zinc are suggested as being the origin of this behavior.

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