Effect of the presence of chlorine in bimetallic PtZn/CeO₂ catalysts for the vapor-phase hydrogenation of crotonaldehyde

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Abstract

The effect of the reduction temperature has been studied on ceria-supported bimetallic platinum-zinc catalysts prepared from H₂PtCl₆ and Pt(NH₃)₄(NO₃)₂ as the platinum precursors and Zn(NO₃)₂ as the zinc precursor. The catalysts have been characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), and X-ray photoelectron spectroscopy (XPS), and their catalytic behavior has been evaluated in the vapor-phase hydrogenation of toluene and of crotonaldehyde (2-butenal) after reduction at low (473 K) and high (773 K) temperatures. The increase in the reduction temperature produces a strong decrease in the catalytic activity for toluene hydrogenation in both systems, but an important increase of activity for crotonaldehyde hydrogenation, which is more evident for the chlorine-free catalyst. The selectivity towards the hydrogenation of the carbonyl bond to yield the unsaturated alcohol (crotyl alcohol, 2-buten-1-ol) also increases after reduction at high temperature, being somewhat higher for the Cl-containing catalyst. The results are discussed in terms of differences in surface composition of the catalysts.

Keywords: PtZn/CeO₂, Selective hydrogenation, XPS, Chlorine effect.

1 Introduction

Rare earth oxides are widely used in heterogeneous catalysis as promoters for noble metal catalysts. Among them, the most significant from the applied point of view is cerium dioxide. It is a very important constituent of three way catalysts (TWC), where it plays a major role as oxygen buffer [1]. Ceria plays also an important role in the removal of SO_x from fluid catalytic cracking (FCC) flue gases and as oxidation catalyst for the removal of soot in the exhaust gases from Diesel engines [2]. Furthermore, it is also used in the removal of water pollutants [3], as an additive in combustion catalysts [4] and in fuel cell technology [5]. The application of CeO_2 in many catalytic processes is based on its unique properties such as: i) the capacity to strongly interact with noble metals after reduction at relatively high temperatures (SMSI effect); ii) beneficial effect on the stabilization of small supported noble metal particles; and iii) the ability to increase the thermal stability of alumina supports. Ceria is able to form oxygen vacancies and intermetallic compounds (M-Ce) after a reduction treatment at relatively high temperatures, and can supply or store oxygen, hydrogen and sulfur, depending on the reaction conditions. This is one of its most important properties that justify its use in three-way catalysts (TWC), which permits the widening of the operative stoichiometric window.

The noble metal-ceria interaction induced after reduction strongly modifies the catalytic behavior of the former. This phenomenon, the so-called strong metal-support interaction (SMSI) effect, has been explained as due to both geometric and electronic effects. Particularly, electronic effects prevail after reduction at temperatures below 773 K on M- CeO_2 systems, while at higher temperatures geometric effects, caused by migration of partially reduced CeO_{2-x} species from the support to the metal particle surface, seem to be more important [6].

The specific metal-support interactions have been used to modify the catalytic behavior of supported noble metal in selective hydrogenation reactions. In this sense, a number of studies have been carried out on the promotion of platinum catalysts with CeO₂ for the selective hydrogenation of α,β -unsaturated aldehydes [7-11]. An increase in the unsaturated alcohol yield in the presence of ceria has been explained on the basis of the formation of anionic vacancies in the M-CeO₂ interface after the reduction treatment at high temperature (about 773 K). The anionic vacancies activate the C=O double bond of α,β -unsaturated aldehydes through the interaction of the oxygen atom of the aldehyde group with the surface oxygen vacancies, thus favoring the hydrogenation of the C=O bond. In the same way, the possibility of electronic effects between the noble metal and the support have to be taken into account to justify the obtained results, as well as the possibility of Pt-Ce alloy formation after a reduction treatment at higher temperatures (about 973 K) [10].

The addition of a second metallic species, more electropositive than platinum, has also been shown to favor enhanced activity and selectivity in the hydrogenation of α,β -unsaturated aldehydes as compared with those of monometallic platinum catalysts. Some examples are Pt-Sn [12-15], Pt-Fe [16] and Pt-Zn [17-22], among others. The effect of the second metal on platinum is enhanced when a partially reducible support and high reduction temperature (773 K) is used, as it has been shown in recent papers [19-22]. As an example, the addition of zinc to Pt/SiO₂ promoted by cerium dioxide produces, after reduction at 773 K, a much more active catalyst with an improved selectivity towards the hydrogenation of the carbonyl bond [19, 20].

This paper compares the surface characteristics and catalytic behavior of Pt-Zn/CeO₂ catalysts prepared from different platinum precursors: H₂PtCl₆ as a chlorinated precursor and Pt(NH₃)₄(NO₃)₂ as a chlorine-free precursor. The role played by chloride

ions on the redox properties of cerium dioxide is well known, and it seems that they can also affect by themselves the catalytic behavior of platinum in the selective hydrogenation of α,β -unsaturated aldehydes. The modification of the catalytic behavior induced by the presence of chloride ions after reduction at low (473 K) and high (773 K) temperatures has been studied in two very different and interesting reactions: toluene hydrogenation and crotonaldehyde hydrogenation. Furthermore, catalysts have been characterized by a number of techniques (XRD, TPR and XPS) in order to try to correlate the surface characteristics of the catalysts with their catalytic behavior in the aforementioned reactions.

2 Experimental

The CeO_2 support was prepared as follows: an aqueous solution of $(\text{NH}_4)_2\text{CO}_3$ was slowly added to a magnetically stirred boiling aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (purity: 99.95%, from Ventron); the white precipitate of cerium carbonate formed was filtered, washed with de-ionized water, and dried overnight at 373 K in air. Then, it was heated in air at $5 \text{ K} \cdot \text{min}^{-1}$ up to 773 K and calcined at this temperature for 4 h. It had a BET surface area of $70 \text{ m}^2 \cdot \text{g}^{-1}$ (N_2 , 77 K). Two different PtZn/CeO_2 catalysts were prepared by co-impregnation using an acetone solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, from Aldrich), and H_2PtCl_6 (99.9%, from Johnson Matthey) for the $\text{Pt}(\text{Cl})\text{Zn/CeO}_2$ and $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ for the $\text{Pt}(\text{N})\text{Zn/CeO}_2$ catalyst, respectively (10 ml of solution per gram of support). The amount of the platinum precursors was the appropriate to obtain a 2wt% Pt loading, whereas 1wt% was the nominal loading for Zn. After 8 h under stirring at room temperature, excess of solvent was removed by flowing N_2 through the suspension. The solids obtained were dried overnight at 373 K and calcined in air at 673 K for 4 h. The metal content was determined atomic absorption spectrometry (AAS).

The platinum content was 1.7 wt% for Pt(Cl)Zn/CeO₂ and 1.8 wt% for Pt(N)Zn/CeO₂. The zinc content in both samples was 0.6 wt%. These values correspond to Zn/Pt ratios of 0.8 and 0.9, respectively.

X-ray diffraction patterns of samples, reduced in flowing hydrogen at 473 and 773 K and then air exposed, were obtained with a JSO Debye-Flex 2002 system, from Seifert, fitted with a Cu cathode and a Ni filter, and using a 2 ° min⁻¹ scanning rate.

Temperature-programmed reduction (TPR) measurements on calcined catalysts were carried out in a U-shaped quartz reactor, using a 5%H₂/He gas flow of 50 cm³·min⁻¹ and about 150 mg of catalyst. Hydrogen consumption was monitored by online mass spectrometry and calibrated by carrying out the reduction of CuO and assuming that it is completely reduced to metallic copper.

X-ray photoelectron spectra (XPS) were acquired with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg K α ($h = 1253.6$ eV, $1 \text{ eV} = 1.6302 \times 10^{-19}$ 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 flowing 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^{-7} N·m⁻² 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. All binding energies (B.E.) were referenced to the C 1s line at 284.6 eV, which provided binding energy values with an accuracy of ± 0.2 eV. The surface Pt/Ce, Cl/Ce and Zn/Pt atomic ratios were estimated from the integrated intensities corrected by the atomic sensitivity factors [23].

The catalysts (100-150 mg, in form of powder) were placed in a U-shaped quartz reactor of 1 cm internal diameter. Before the determination of their catalytic behavior, they were reduced *in situ* under flowing hydrogen ($50\text{ cm}^3\cdot\text{min}^{-1}$) at 473 or 773 K for 10 h, at a heating rate of $5\text{ K}\cdot\text{min}^{-1}$. 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 performed at 353 K. The reduced catalysts were contacted with a reaction mixture (total flow: $50\text{ cm}^3\cdot\text{min}^{-1}$; H_2/CROALD ratio of 26) formed by passing a hydrogen flow through a thermostabilized saturator (293 K) containing the unsaturated aldehyde. Both reactions were carried out at atmospheric total pressure. In both cases, the reaction products were analyzed by online gas chromatography, using a Carbowax 20M 58/90 25 to 30-m capillary column to separate the reactants and the reaction products.

3 Results and discussion

3.1 Catalyst Characterization

Figure 1 shows the X-ray diffraction patterns of catalysts $\text{Pt}(\text{Cl})\text{Zn}/\text{CeO}_2$ and $\text{Pt}(\text{N})\text{Zn}/\text{CeO}_2$ after reduction in flowing hydrogen at low (473 K) and high (773 K) temperature and then being air exposed. It can be seen that, from the structural point of view, the reduction treatments applied affect both catalysts in a similar way. Thus, the X-ray diffraction profiles show four diffraction peaks, at $2\theta = 28.5^\circ$, 33.1° , 47.4° and 56.4° , corresponding to the fluorite phase of ceria. Curiously, these diffraction peaks are somewhat wider after reduction at high temperature. Similar results have been previously described in the literature [7-9, 26]. X-Ray diffraction (XRD) studies on $\text{Pd}(\text{Cl})/\text{CeO}_2$ catalysts reduced at different temperatures [26] showed that the diffraction peaks corresponding to the fluorite phase of CeO_2 became wider as the reduction

temperature was increased, with a drastic change after reduction at 773 K, and this was assigned to the occurrence of new diffraction peaks corresponding to tetragonal CeOCl. But these authors also observed different ceria phases depending on the presence of metal and on the reduction temperature, and irrespective of the presence of chlorine: a CeO_{2-y} fluorite structure and a distorted CeO₂ structure with pseudo-cubic structure. The close proximity of the diffraction peaks corresponding to these structures could be envisaged as a broadening of the diffraction peaks of the ceria support. In conclusion, an increase in the reduction temperature from 473 K to 773 K produces a small broadening of the CeO₂ diffraction peaks which is assigned to the formation of new reduced ceria phases with diffraction peaks appearing close to those from the CeO₂ phase. No reflections due to Pt, Zn or Pt-Zn species could be detected, what is indicative of a high metal dispersion degree.

Figure 2 shows the temperature-programmed reduction profiles (H₂ consumption) obtained for both catalysts. The TPR profiles of the catalysts exhibit two main peaks. For the chlorinated catalyst there is a sharp peak centered at 577 K, which is assigned to the surface reduction of ceria in close contact with the metal, as well as to the breakdown of Pt-O-CeO₂ species formed upon calcination and, probably, the reduction of zinc species. The second broad peak at higher temperatures (with maximum at about 1218 K) is related to the bulk reduction of the support and this feature also appears in the TPR profile obtained with the chlorine-free catalyst. However, in the low temperature region, the TPR profile obtained with the chlorine-free catalyst shows a broad hydrogen consumption that takes place between 350 and 700 K, which may be deconvoluted into three contributions, the main one centered at 540 K and two shoulders at lower temperatures (460 and 490 K). This broad reduction peak includes the surface reduction of ceria in close contact with the metal, and may also

include the reduction of platinum and/or zinc species. Furthermore, the broadness of this peak as compared to that obtained for the chlorinated catalyst indicates a much higher surface heterogeneity in the absence of chloride ions. It is noticeable the fact that the surface reduction takes place at a lower temperature in the chlorine-free catalyst. A similar result has been recently reported in a study on the influence of the precursor salt on metal particle formation in Rh/CeO₂ catalysts [27], where it was observed that the presence of chloride ions delayed rhodium reduction and hindered the onset of the metal-support interactions. These observations were explained as due to chloride ions at the metal-support interface hindering electron exchange between the metal and the oxide support. Finally, a broad feature appears for both catalysts between 750 and 900 K, and can be assigned to the surface reduction of support not in close contact with platinum.

The Pt 4f level X-ray photoelectron spectra for the as-prepared (calcined) and reduced catalysts are compared in Figures 3a (chlorinated catalyst) and 3b (chlorine-free catalyst). For both catalysts, independently of the reduction treatment, two broad bands are present which correspond to the Pt 4f_{7/2} and Pt 4f_{5/2} levels. In a first approach, charge effects on the samples could originate the broadness of the bands during the XPS measurements, as they were not compensated by the use of a flood gun. However, the wideness of the peaks may also be due to the overlapping of individual peaks corresponding to platinum species with slightly different electronic states. Actually, the broad experimental peaks are not strictly symmetrical, which could be explained by different contributions of individual peaks. Therefore, the main experimental Pt 4f_{7/2} peak has been deconvoluted into different components. Their binding energies and their relative contributions to the main peak, as well as the Pt/Zn, Pt/Ce, Zn/Ce and Cl/Ce

atomic ratios, are reported in Table 1. Furthermore, the Zn LMM kinetic energies in both catalysts after the different reduction treatments are also reported in Table 1.

For the as-prepared Pt(Cl)Zn/CeO₂ catalyst a broad signal with contributions at 70.4, 72.4 and 74.0 eV, corresponding to metallic platinum and different oxidized platinum species, respectively, has been obtained. The reduction treatment at 473 K originates a shift of the contribution at the lowest binding energy (attributed to metallic Pt) to a value which is higher than in the calcined catalysts: 71.5 eV. The peak at 72.7 eV still indicates the presence of Pt(II) species. After reduction at 773 K both peaks remain in their respective positions, although the contribution of that with the lowest binding energy increases from 49% to 59%, this indicating a higher reduction degree of platinum.

Regarding the chlorine-free catalyst, the XPS spectra obtained with the as-prepared sample shows a broad band (Figure 3b), which has been deconvoluted into three contributions at 71.8, 72.8 and 73.9 eV, assigned to different oxidized platinum species. Thus, there is no contribution that could be clearly assigned to metallic platinum in this calcined catalyst. After the reduction treatments at 473 and 773 K the contribution at 73.9 eV disappears, and the binding energies of the two remaining bands are not modified, although the relative contribution of that placed at a lower binding energy (71.8 eV) is increased.

The possibility of PtZn alloy formation in these systems (evidenced by XRD diffraction) has been addressed by several authors [17, 26] as depending on the metal precursor and the reduction temperature. The X-ray diffraction patterns obtained in the present research do not allow to discern any diffraction peak that could be ascribed to Pt, Zn, or a PtZn alloy, maybe due to the lower metal contents and to a high metal dispersion. The higher binding energies of the platinum 4f_{7/2} transition in the reduced

catalyst (71.5, 71.8 eV) compared to those obtained in Pt monometallic catalysts or in the calcined unreduced samples (70.4 eV) could be originated by the interaction between platinum and zinc atoms (see Table 1). In this sense, Rodriguez and Kuhn [27], using CO adsorption, suggested that the formation of Pt-Zn bonds produces a large depletion in the density of Pt 5d states around the Fermi level, with a shift in the center of the Pt 5d band and 4f core levels toward higher binding energies. These higher binding energies could also be due to particle size effects (small metallic crystallites), although the surface Pt/Ce ratios obtained by XPS (Table 1, see below) indicate a similar Pt dispersion. The interaction of platinum with the ceria support could also produce high binding energy values. It is worth to mention that complete platinum reduction after treatment at 773 K, which is common when other supports are used (silica, alumina, carbon), is not achieved here, with a high amount of platinum remaining in an electron deficient state. However, the Pt binding energies are not modified by an increase in the reduction temperature which, in turn, is able to induce the SMSI state.

The binding energies of the Zn 2p_{3/2} transition do not permit to discern the oxidation state of zinc. The spectra show a single band centered at 1022.4 ± 0.4 eV, without any appreciable tendency. The difficulty of assessing the oxidation state of zinc by XPS measurements is well recognized in the literature, as the binding energies of metallic and oxidized Zn are very close. In this case, it is necessary to take into account the analysis of the Zn LMM Auger transition, which is more sensitive to oxidation state of zinc [28]. The Zn LMM kinetic energies for both catalysts, after different treatments, are reported in Table 1. In both cases, the Auger spectra show the absence of metallic zinc in the calcined catalysts (band centered at 988.1 eV, assigned to Zn(II) species). The reduction treatment at low temperatures produces a single contribution at a kinetic energy of 991.7 eV, attributed to metallic Zn. The kinetic energy is similar for the

chlorinated catalyst after the reduction treatment at 773 K, although is it shifted further (to 991.4 eV) in the chlorine-free sample. In accordance with XPS measurements related to Pt 4f_{7/2} transition, this shift in Zn LMM kinetic energies after the reduction treatment could be an indication of some Pt-Zn interaction or alloy formation.

The oxidation state of cerium in the two catalysts after the different reduction treatments have been assessed as described elsewhere [9], and the values obtained are reported in Table 1. As it can be seen, there is some ceria in a reduced state (Ce(III)) even in the calcined unreduced catalysts: 21.7 and 17.0 % for the chlorinated and for the chlorine-free catalyst, respectively. This has been shown to be due to the high energy X-ray flux impinging onto the sample [9, 29, 30]. A slight increase in the amount of reduced surface ceria is observed in both cases after the reduction treatment at 473 K, the %Ce(III) increasing up to 22.5 and 20.6 for the chlorine-containing and chlorine-free catalyst, respectively. Reduction at higher temperature does not produce a significant effect on the chlorine-free catalyst, but the amount of Ce(III) is highly increased for Pt(Cl)Zn/CeO₂, from 22.5 to 30.0%. Previous XPS studies on Pt/CeO₂-SiO₂ and PtZn/CeO₂-SiO₂ catalysts [9], prepared from the chlorine-free precursor, showed a similar behavior than that described for the Pt(N)Zn/CeO₂ catalyst, although the extent of the ceria partial reduction was higher in the former as it could be expected for a supported ceria catalyst (smaller crystal sizes as obtained from XRD analysis). According to these results, and considering that both samples have been submitted to the same treatments, the higher amount of Ce(III) observed after reduction of Pt(Cl)Zn/CeO₂ at 773 K can be tentatively attributed to the presence of chlorine and, more specifically, to the formation of CeOCl species. Le Normand *et al.* [31] described the formation of the oxychlorine phase on a Pd(Cl)/CeO₂ catalyst after a reduction treatment at 673 K. No definitive changes were observed by XRD and XPS analysis, the

only evidence of a structural modification being the molar Cl/Ce ratio close to one, but just for low ceria content. Table 1 reports the Cl/Ce ratios for Pt(Cl)Zn/CeO₂ in the calcined (unreduced) and reduced states. Taking into account the Cl/Ce ratio after the reduction treatment at 773 K, when those changes have been observed, the value 0.2 is quite different from 1, reported in the literature. However, due to the low chlorine content (because of the low platinum content) in this catalyst, as well as to the presence of bulk ceria in the support, it would be reasonable to expect the CeOCl microphases formation just on a small fraction of the surface. It is interesting to mention the high chlorine enrichment observed on this catalyst after the high reduction temperature treatment (Cl/Ce ratio of 0.14 for the catalyst reduced at 473 K and 0.2 after reduction at 773 K). This increase in the chlorine surface concentration, together with the higher reducibility of ceria in the chlorine-containing catalyst, is another evidence of the critical chlorine effect on the catalyst surface after the high temperature reduction treatment.

The XPS atomic Pt/Ce and Zn/Ce ratios of the two samples after different treatments can be used as an estimation of dispersion for both metals (Table 1). The Pt/Ce ratios are very similar in both unreduced catalysts (0.038 and 0.039), this pointing to a similar dispersion. A first reduction treatment at 473 K produces a platinum surface enrichment with an increase in Pt/Ce ratios to 0.047 and 0.045 for the chlorine-containing and chlorine-free catalysts, respectively. A further reduction at 773 K suddenly decreases the ratio in both samples. A similar effect is observed for zinc. Atomic Zn/Ce ratios increase after the low temperature reduction and sharply decrease after the 773 K reduction treatment. This decrease is more pronounced for the chlorine-free catalyst. The sintering of the metallic species under these reduction conditions and

a dilution effect originated by the interaction between the two metals could explain this result.

3.2 Catalytic behavior

The assessment of the metallic dispersion on ceria-based catalysts using gas adsorption measurements is not easy. The ability of ceria to chemisorb hydrogen and CO at room temperature produces an overestimation of the amount of surface metal exposed [31, 32]. An estimation of the amount of platinum surface atoms in these systems can be achieved by determining their catalytic activity in a structure-insensitive reaction. In this way, benzene hydrogenation [33] and toluene hydrogenation [9] have been recently used to fulfill this objective. Thus, Fajardie et al. [33] obtained a good correlation between the amount of exposed metal atoms determined by benzene hydrogenation, and calculated from hydrogen chemisorption in chlorine-containing catalysts, where hydrogen spillover from the metallic particle to the ceria support is inhibited. Benzene hydrogenation measurements gave more accurate results of the total amount of exposed atoms in the case of chlorine-free catalysts. Also, cyclohexane dehydrogenation has been used as a structure-insensitive reaction for the assessment of accessible metal atoms in model three-way catalysts [34]. However, despite the structure-insensitive character of these reactions, it is necessary to consider that the catalytic activity can be modified by metal-support interactions (SMSI) or by electronic effects arising from other metallic species present on the catalyst surface.

The effect of the reduction temperature on the catalytic activity of the Pt(Cl)Zn/CeO₂ and Pt(N)Zn/CeO₂ for toluene hydrogenation was tested at 333 K, after treating the catalysts in flowing hydrogen at 473 or 773 K. Catalytic activity in the two samples is very low irrespective on the reduction temperature, with conversion degrees

lower than 1%. Although the chlorine-free catalyst is somewhat more active than its counterpart (2.7 vs. 1.5 μmol of methylcyclohexane $\cdot \text{s}^{-1} \cdot \text{gPt}^{-1}$) both of them became nearly inactive after reduction at 773 K. Previous studies on the catalytic behavior of Pt/CeO₂-SiO₂ and PtZn/CeO₂-SiO₂ samples in toluene hydrogenation reaction have shown a severe decrease of the catalytic activity after Zn addition, even after a low temperature reduction treatment, when strong metal-support interaction is not expected [9]. This decrease is related to the dilution and/or the coverage of surface platinum atoms by zinc species. It has to be noticed that, in spite of the fact that the chlorine-free catalysts shows the lower amount of surface platinum after reduction at 473 K (see Table 1), it is more active than its counterpart. As this reduction temperature is too low to induce any support interaction, it can be concluded that the platinum-zinc interaction is lower in the absence of chlorine. Results obtained after reduction at 773 K are more difficult to explain, as they are now a result of the platinum-zinc interaction and also of the strong interaction of platinum with the ceria support. Indeed, the chlorine-free catalyst is inactive in spite of the low amount of surface zinc detected by XPS.

The effect of the presence of chlorine and reduction temperature on the catalytic behavior of these catalysts in the vapor-phase hydrogenation of crotonaldehyde is completely different from that observed in toluene hydrogenation. Figures 4a and 4b show the evolution of the overall activity (μmoles of crotonaldehyde transformed per gram of platinum and second) of catalysts Pt(Cl)Zn/CeO₂ and Pt(N)Zn/CeO₂ in this reaction as a function of time on stream at 353 K, after being reduced at 473 (Fig. 4a) or 773 K (Fig 4b). Conversion degrees at the beginning and at the end of the reaction are include in the Figures. Values reported have been obtained once the carbon balance have been achieved, i.e., when the amount of crotonaldehyde leaving the reactor matches that fed minus that transformed into the products. After an important

deactivation during the first 30 or 60 minutes (depending on the reduction treatment applied) on reaction, which is more pronounced after reduction at high temperature, the activity remains rather stable with time on stream. The chlorine-containing catalyst, reduced at 473 K (Figure 4a), shows a stable activity after the initial deactivation close to $5 \mu\text{mol of crotonaldehyde} \cdot \text{gPt}^{-1} \cdot \text{s}^{-1}$ from an initial value of about 14. When the reduction treatment was carried out at 773 K (Fig 4b) an important improvement in the initial activity, of around threefold, is observed. Even although a stronger deactivation takes place with time on stream, the catalytic activity remains higher than after reduction at lower temperature.

The increase in catalytic activity when the reduction temperature is increased to 773 K was also observed in a previous study on the title reaction over Pt/CeO₂ prepared with a chlorinated platinum precursor (H₂PtCl₆) [7]. On the other hand, a Pt/CeO₂-SiO₂ catalyst (prepared in the same conditions) showed a decrease in catalytic activity when the reduction temperature was increased. This allows to conclude that ceria, and the strong metal-support interaction induced after reduction at 773 K, are the origin of the increased catalytic activity, the effect being more important as the amount of ceria in the support is increased (bulk ceria in Pt/CeO₂ and Pt(Cl)Zn/CeO₂ vs. supported ceria in Pt/CeO₂-SiO₂).

The same effect of the reduction temperature is obtained for the chlorine-free catalyst, although the increase of activity after reduction at high temperature is much more important in this case. After the low temperature reduction treatment, the catalytic activity is nearly constant and centered at around $10 \mu\text{mol of crotonaldehyde} \cdot \text{gPt}^{-1} \cdot \text{s}^{-1}$ (slightly higher than with the ex-chloride catalyst). However, the increase in the reduction temperature to 773 K produces an improvement on the initial catalytic activity of more than sevenfold over that obtained for the Pt(Cl)Zn/CeO₂ sample. After 120 min

on stream the activity reaches a value of about $50 \mu\text{mol of crotonaldehyde} \cdot \text{gPt}^{-1} \cdot \text{s}^{-1}$, which is five times higher than that obtained for the chlorine-based catalyst in the same reaction conditions.

The differences between both catalysts are also evident in terms of selectivity. The products obtained under the conditions used in this study are butyraldehyde (hydrogenation of the C=C bond), crotyl alcohol (but-2-en-ol, formed by the hydrogenation of the carbonyl C=O bond), butanol (hydrogenation of the primary products butyraldehyde and crotyl alcohol), and the light hydrocarbons. In the case of the catalysts presented in this paper, butanol is not detected, and the amount of light hydrocarbons is similar in both runs, irrespective of the reduction temperature treatment, and is lower than 5% molar fraction and diminishing with stream time. Consequently, a high selectivity to crotyl alcohol means a low selectivity for the hydrogenation of C=C bond yielding butyraldehyde.

The selectivity to crotyl alcohol (CROALC) (% molar fraction) is plotted in Figure 5 as a function of time on stream at 353 K, after reduction at both low (473 K) and high (773 K) temperatures. Both catalysts, Pt(Cl)Zn/CeO₂ y Pt(N)Zn/CeO₂ show, after reduction at 473 K, a selectivity to CROALC lower than 10% at conversion values of about 2%. Selectivity decreases with time on stream, reaching a nil value (100 % selectivity to butyraldehyde) after only 25-30 min on stream. This behavior is similar to that obtained with Pt/CeO₂-SiO₂ and PtZn/CeO₂-SiO₂ [9]. However, reduction at high temperature produces a strong increase in selectivity to CROALC, with maxima values of 30 and 40 % for the chlorinated and chlorine-free catalyst, respectively. Again, the behavior is analogous to that obtained with a chlorine-free PtZn/CeO₂-SiO₂ catalyst [9] although, in this case, the maximum selectivity obtained was slightly higher (40% vs. 30% for the catalyst reported in this paper). In this sense, it has to be noted that the

Zn/Pt bulk atomic ratios of both catalysts are also different, being lower for the catalyst reported in this paper (0.9 vs. 1.6).

After reduction at low temperature both catalysts behave in a similar way in terms of activity and selectivity. It is after reduction at 773 K when the differences appear. The catalytic activity increases in both cases, but to a greater extent for the chlorine-free catalyst. On the other hand, the selectivity towards the unsaturated alcohol also increases after reduction at high temperature, but now the maximum values are obtained with the chlorinated catalyst.

Different interactions can take place in this complex system which determine its catalytic behavior. It seems clear from previous studies that CeO₂ enhances both the catalytic activity and the selectivity towards the hydrogenation of the carbonyl bond after reduction at high temperature [7-10]. The effect of the residual chlorine on ceria based catalysts has been reported to affect different processes such as H₂ and CO chemisorption [35], benzene hydrogenation [33], and selective hydrogenation of crotonaldehyde [10, 11]. Abid et al. [10] observed the formation of CePt₅ particles in a chlorine-free Pt/CeO₂ catalyst, after reduction at 973 K, which provided more than 80% crotyl alcohol selectivity. This phenomenon did not happen in the chlorine-containing catalyst, which yielded lower selectivity values. The formation of Pt-Ce alloy phases has not been observed at 773 K, the higher reduction temperature used in this study, but the modification of the redox properties of the ceria surface by the presence of chlorine is well reported in the literature. In fact, chlorine ions from the metallic precursor move to the ceria support during the reduction treatment, producing the replacement of O²⁻ ions to form CeOCl species. In this way, the CeOCl microphases block the oxygen vacancies, thus inhibiting both the direct and the back hydrogen spillover processes. In this sense, the positive promoter effect of ceria after reduction at high temperature could

be attenuated in the Pt(Cl)Zn/CeO₂ catalyst, this being the origin of its lower catalytic activity after reduction at 773 K as compared to the Cl-free catalyst.

The presence of Zn introduces a new parameter. It has been shown that it can strongly modify the catalytic behavior of platinum in this kind of systems [9], and also in the absence of ceria. Touroude et al. [17, 36] studied the catalytic behavior of Pt/ZnO catalysts, prepared from H₂PtCl₆ and Pt(NH₃)₄(NO₃)₂ as the platinum precursor, in the gas phase hydrogenation of crotonaldehyde. They found that the ex-chloride catalyst was much more active and selective, achieving up to 90 % crotyl alcohol selectivity under certain conditions. The results were explained on the basis of PtZn alloy formation, which was shown to be easier (i.e., it occurred at a lower temperature) in the ex-chloride catalyst, and of the increase of the surface acidity of the ZnO support induced by the presence of chlorine which, in turn, could influence the electronic properties of the platinum particles.

From the results obtained in this study it can be concluded that the presence of chloride ions increases the reducibility of the ceria support, as a higher percentage of Ce(III) has been obtained by XPS (Table 1). However, the catalytic activity after reduction at high temperature is higher in the chlorine-free catalyst. It could be due to the blocking effect of chloride ions on the formation of oxygen vacancies at the ceria surface which would promote the hydrogenation of the carbonyl bond through its interaction with the oxygen atom by acting as Lewis acid centers. With regards to the effect of Zn, it can be assumed that the presence of chlorine favors its interaction with platinum. This is supported by differences in the TPR profiles of both catalysts (Figure 2), with a narrower peak of hydrogen consumption for the chlorine-containing sample. Furthermore, the Pt/Zn XPS atomic ratio obtained after reduction of the chlorine-free catalyst at high temperature is much higher (1.22) than that of its counterpart (0.35), this

pointing to segregation and sintering of zinc particles. This could be the origin of the much higher activity of the Pt(N)Zn/CeO₂ catalyst after reduction at high temperature. Its slightly lower selectivity could also be due to the lesser extent of the platinum-zinc interaction in the absence of chlorine.

4 Conclusions

The use of different platinum precursors, H₂PtCl₆ and Pt(NH₃)₄(NO₃)₂, to prepare bimetallic Pt-Zn catalysts supported on CeO₂ yields catalysts with distinctive catalytic behavior in the vapor-phase hydrogenation of crotonaldehyde. The presence of chloride ions increases the reducibility of the ceria support, but diminishes its promoter effect maybe due to the formation of surface Ce-O-Cl species. On the other hand, it favors the platinum-zinc interaction, this being positive for enhancing the catalytic selectivity towards the hydrogenation of the carbonyl bond to yield the unsaturated alcohol. As a result, catalyst reduced at 773 K are much more active than after reduction at 473 K due to the partial reduction of the ceria surface, the effect being more accentuated in the Cl-free catalyst. On the other hand, the chlorine-free catalyst shows a somewhat lower selectivity to crotyl alcohol (the unsaturated alcohol), which can be explained by a lower Pt-Zn interaction.

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Table 1. Catalyst Characterization by XPS

Catalyst	T _{Red} (K)	Pt/Ce	Pt/Zn	Zn/Ce	Cl/Ce	B.E. Pt 4f _{7/2} (eV)	K.E. Zn LMM (eV)	Ce(III) (%)
Pt(Cl)Zn/CeO ₂	----	0.038	0.54	0.071	0.15	70.4 (28)	988.2	21.7
						72.4 (60)		
						74.0 (12)		
	473	0.047	0.39	0.118	0.14	71.5 (49)	991.7	22.5
						72.7 (51)		
	773	0.034	0.35	0.098	0.20	71.5 (59)	991.8	30.0
Pt(N)Zn/CeO ₂	----	0.039	1.14	0.035	----	71.8 (26)	988.8	17.0
						72.8 (23)		
						73.9 (51)		
	473	0.045	0.31	0.144	----	71.8 (49)	991.7	20.6
						72.8 (51)		
	773	0.030	1.22	0.025	----	71.8 (63)	991.4	20.3
						73.0 (37)		

Table Captions

Table 1. Catalyst Characterization by XPS.

Figure Captions.

Figure 1. X-ray diffraction patterns of catalysts Pt(Cl)Zn/CeO₂ and Pt(N)Zn/CeO₂, reduced at 473 and 773 K.

Figure 2. TPR curves (H₂ consumption) for Pt(Cl)Zn/CeO₂ (full line) and Pt(N)Zn/CeO₂ (dotted line) catalysts.

Figure 3. XPS Pt 4f spectra of the as-prepared (calcined) and reduced catalysts. (a) Pt(Cl)Zn/CeO₂; (b) Pt(N)Zn/CeO₂

Figure 4. Evolution of catalytic activity for crotonaldehyde hydrogenation with time on stream at 353 K for catalysts Pt(Cl)Zn/CeO₂ (○) and Pt(N)Zn/CeO₂ (■) after reduction at 473 K (a) or 773 K (b).

Figure 5. Evolution of selectivity to crotyl alcohol with time on stream at 353 K for catalysts Pt(Cl)Zn/CeO₂ (●○) and Pt(N)Zn/CeO₂ (■□) reduced at 473 K (solid symbols) and at 773 K (open symbols).

Figure 1

Figure 2

Figure 3a

Figure 3b

Figure 4a

Figure 4b

Figure 5