Selective Hydrogenation of Citral with Carbon Nanotubes Supported Bimetallic Catalysts Prepared by Deposition–Reduction in Liquid Phase and Conventional Impregnation Methods

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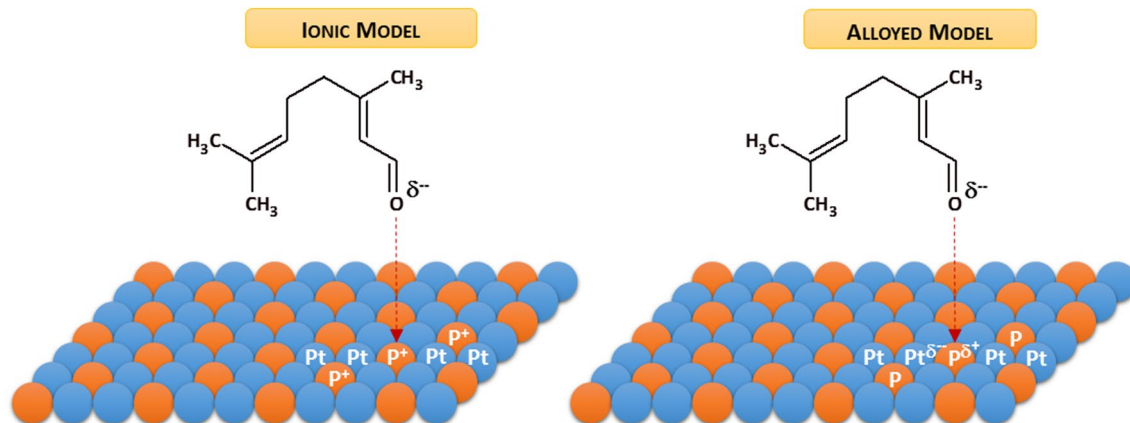
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Abstract This paper studies the preparation of Pt-based bimetallic (PtFe, PtSn, PtIn and PtGa) catalysts supported on carbon nanotubes for the citral hydrogenation by deposition–reduction in liquid phase and their comparison with the conventional impregnation method (CI). When conventionally impregnated, the selectivity to unsaturated alcohols (UA) highly increased from the monometallic to the bimetallic samples, whereas for liquid phase reduced ones, the selectivity to UA was rather similar for both Pt and bimetallic samples except for PtFe ones and for the PtSn catalyst treated treated with N_2. The results were explained taken into account the intimate interaction achieved between the metals according to the preparation method and the formation of Pt–promotor complexes in the impregnating solution.

Graphical Abstract

1 Introduction

Bimetallic catalysts are widely used in the selective hydrogenation of the carbonyl group of α,β-unsaturated aldehydes into α,β-unsaturated alcohols (UA) [1, 2]. The challenge is to achieve the hydrogenation of the carbonyl group

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(C=O) without affecting the olefinic bond (C=C) which is thermodinamically favoured and usually low yields are obtained with typical monometallic catalysts [1, 3]. For these bimetallic catalysts, it is known that the final selectivity of the active metallic phase depends both on the second metal/noble metal ratio and the interaction between the active metal and the reduced or ionic species of the second metal acting as Lewis acid sites to promote the hydrogenation of the carbonyl group [4–6]. Besides, it is the nature of the support that plays an important role as well as the preparation method.

The simplest way to prepare supported bimetallic catalysts is the conventional impregnation (CI), either by coimpregnation or successive impregnation of the support material with a solution of metal precursors followed by a reduction step at high temperature under hydrogen flow [7, 8]. In these cases, the final interaction between the components depends on the catalytic support. A better control of the composition of the bimetallic particles can be achieved through surface modification of supported platinum particles with organometallic compounds [9]. Although this method has been widely studied, for example, with tin and germanium organometallic compounds [9, 10], in many cases the change in the selectivity of the reaction is not as significant as expected, probably because theses compounds only selectively modifies the active metal avoiding the deposition of the second metal onto the support and the poisoning of acid sites responsible of undesirable side reactions. Also, the co-reduction of the metal ions from the liquid phase at moderate temperatures by applying reducing agents and the deposition of them on the support can be used to produce bimetallic catalysts [11, 12]. The reduction in liquid phase method (RLP) is widely used to prepare electrocatalysts for fuel cells on carbonaceous materials, but less studied to prepare catalysts for selective hydrogenation. Althought the RLP method seems to be more flexible with respect to the involved variables (such as type of reducing agent, and deposition and reduction conditions) in the steps of preparation in relation to the CI method, for selective hydrogenation the information about the effect of the preparation method on the catalytic behavior, and specifically in relation to other methods is scarce. For example, Liu et al. [13] evaluated Pt catalysts prepared by RLP in the selective hydrogenation of cinnamaldehyde to the corresponding UA and explained the results obtained according to the electronic and structural effects present in the different types of nanotubes used, regardless of some influence of the preparation method. Guo et al. [14] reported a nonoxidative funtionalization method of nanotubes using acrylic acid to create preferred nucleation sites for the anchoring Pt and Ni metallic precursor, which were then reduced in liquid phase using a reducing agent and with the addition of ionic salts to change the morphology of the

metallic crystals [15–17]. On the other hand, Serrano-Ruiz et al. [17], Pt catalysts supported on carbon were prepared by two deposition and reduction in liquid phase methods to obtain catalysts with polyoriented or (100) and (111) preferentially oriented Pt particles. In both cases, the morphologies of the particles were correlated with the selectivity obtained in the hydrogenation of α,β-unsaturated aldehydes into α,β-unsaturated alcohols. The results showed a structure-sensitive character according to the particle morphology as it was expected from theoretical aspects [14, 18–20] but the selectivities reached to UA were very low and less important, probably due to the use of monometallic catalysts. Regarding bimetallic catalysts, Li et al. [21], prepared PtCo bimetallic catalysts supported on carbon nanotubes by different impregnation techniques (using different metallic precursors and order of addition of metals) and different reduction methods (H_2 flow, HCHO and KBH_4 reducing agent). The results obtained in the cinnamaldehyde selective hydrogenation showed that the different deposition and reduction methods of metallic ions have an important influence on the activity and selectivity of the reaction. Other study, was reported by Guo et al. [22], with bimetallic catalysts wich were prepared by a concomitant deposition step of Pt and a second metal (Mn, Ni, Cu, Zn, Sn, Fe, Co) on carbon nanotubes following of the Pt reduction step using ethylene glycol in a microwave reactor. Even though the microware-assisted polyol reduction is said to improve the interaction between metals, the selectivity to UA obtained from cinnamaldehyde was similar to homologous catalysts prepared by conventional impregnation. Besides, in the two last studies, the correlation between the catalytic performance and metallic phase properties evidenced from characterization results for bimetallic catalyst is not clear.

In this work Pt-based bimetallic catalysts were prepared by two different techniques and the effect of the preparation method on the catalytic behavior in the selective hydrogenation of α,β-unsaturated aldehydes to α,β-unsaturated alcohols was studied. Citral was chosen as model molecule because it is an interesting α,β-unsaturated aldehyde obtained from an abundant raw material (lemongrass oil) and whose C=O group monohydrogenation products (unsaturated alcohols) are very important in flavoring and perfumery industries [23, 24]. Multiple wall carbon nanotubes were selected as catalytic support taking into account their good textural properties to deposit metals and their exceptional physico-chemical properties [25]. Thus, this work refers to the study of the behavior of two series of PtFe, PtSn, PtGa and PtIn bimetallic catalysts prepared both by conventional impregnation and deposition–reduction in liquid phase methods in relation to the production of the unsaturated alcohols from citral (geraniol and nerol).

2 Experimental

Commercial multiple wall carbon nanotubes (MWCN from Sunnano, purity>90%, diameter: 10–30 nm, length: 1–10 μm) were purified according to the technique reported in a previous work [26].The impurity content of carbon nanotubes was dramatically reduced up to 0.45 wt% (Fe: 0.2136; Cl: 0.2349; Al: 0.0111; Si: 0.0103; S: 0.0036; Cr: 0.0031; Ca: 0.0029; Ni: 0.0025; and K: 0.0007 wt%). The so-purified support was name CNP. Textural properties (S_{BET}, Vpore) of both supports (CN and CNP) as well as isoelectric point (IP) and caracterization of surface chemistry were determined and reported elsewhere [27]. Purified carbon nanotubes showed a IP=4.7 and an amphoteric behavior. For this support, the purification treatment mainly produces the formation of weak acid groups. Previous results reported that CNP display a very good adsorption of the metals during the impregnation step [27].

2.1 Preparation of the Catalysts

2.1.1 Conventional Impregnation

The monometallic catalyst was prepared by conventional impregnation of the support CNP using an aqueous solution of H_2PtCl_6 according to the techniques reported elsewhere [28, 29]. Bimetallic catalysts were prepared by successive impregnation of the Pt monometallic one with the corresponding precursors ($FeCl_3$, $SnCl_2$, $Ga(NO_3)_3$ or $In(NO_3)_3$) using the same conditions used to obtain the monometallic catalyst. Table 1 shows the concentration and denomination of the catalysts.

After impregnation, catalysts were reduced at 350 °C under hydrogen flow for 3 h in a flow reactor. Additionaly, after the reduction step catalysts were submitted to another thermal treatment to induce a sinterization and/or modification of the metallic phase. They were treated with nitrogen flow at 700 °C for 12 h [27]. These catalysts were referred in the text by $–N_2$.

2.1.2 Deposition and Reduction in Liquid Phase

Mono and bimetallic catalysts were prepared by deposition and reduction in liquid phase using sodium borohydride ($NaBH_4$) as reducing agent. The support was impregnated with an aqueous solution of the H_2PtCl_6 precursor (in the case of the monometallic catalysts) or the H_2PtCl_6 and the corresponding second metal (in the case of bimetallic catalysts) followed by a reduction step with the addition of $NaBH_4$ in NaOH (1 M), using a volume of impregnation/mass of support ratio of 30 mL g^{-1} according to the technique described elsewhere [29, 30]. A redicibility test was carried out with KI and a colour indicator [11, 30].

Additionally, the catalysts were submitted to a thermal treatment in order to induce a sinterization and/or modification of the metallic phase which consisted in submitting the catalysts under N_2 flow at 700 °C for 8 h. These catalysts were referred in the text by $–N_2$.

2.2 Citral Hydrogenation

The citral hydrogenation was carried out according to the technique described elsewhere [7, 27], the solvent also being 2-propanol.Prior to the reaction, only the catalysts prepared by CI, were reduced "in-situ" under flowing H_2 at 350 °C for 3 h. The reaction products were analyzed in a GC system with a capilar column (Supelcowax 10M) and a FID detector. The catalytic activity was defined as the sum of percentages of citral converted into different products. The selectivity to a given product (i) was calculated as the ratio between the amount of product i and the total amounts of products.

Table 1 Concentration and denomination of the studied catalysts

Catalysts designation	Preparation method	Pt loading (wt%)	P loading (wt%)	P/Pt atomic ratio
Pt/CNP–CI	Conventional impregnation	5.00	–	–
PtFe/CNP–CI			2.50	1.75
PtSn/CNP–CI			1.00	0.33
PtGa/CNP–CI			1.80	1.00
PtIn/CNP–CI			2.50	0.85
Pt/CNP–RLP	Deposition and reduction in liquid phase	5.00	–	–
PtFe/CNP–RLP			2.50	1.75
PtSn/CNP–RLP			1.00	0.33
PtGa/CNP–RLP			1.80	1.00
PtIn/CNP–RLP			2.50	0.85

P promoter loadings dates from references [32, 33]

2.3 Characterization of the Catalysts

Three test reactions were used to characterizate the metallic phase of the catalytic samples: cyclohexane dehydrogenation (CHD), benzene hydrogenation (BH) and cyclopentane hydrogenolysis (CPH). The reactions were performed in a differential continuous flow reactor at atmospheric pressure by using a H_2 volumetric flow of 600 mL min^{-1}. For CHD the reaction temperature was 250 °C and the H_2/CH molar ratio equal to 26.5, for BH the reaction temperature was 110 °C and the H_2/B molar ratio equal to 21.8, and for CPH the temperature was of 350 °C and the H_2/CP molar ratio equal to 23.1. For the CHD and CPH reactions the catalysts were previously reduced "in situ" in flowing H_2 at 350 °C for 3 h; for the BH reaction the catalysts were heated in H_2 flow up to the corresponding reaction temperature. The weight of the samples used in these test reactions was the appropiate one to obtain a conversion lower than 5% (differential flow reactor). The reaction products and the remaining reactants were analyzed by using a gas chromatographic system. The activation energy values for CHD (Ea_{CH}) and BH (Ea_B) were calculated by linear regression using the reaction rates measured at three temperatures and the Arrhenius plot (ln r^0_{CH} vs. $1/T$ (K^{-1})). Specifically, the reaction temperature values used in these measurements for CHD were 250, 240 and 230 °C, and for BH, 110, 100, and 90 °C.

Temperature programmed reduction (TPR) experiments were performed by using a reductive mixture of H_2 (5%v/v)-N_2 and a flow rate of 9 mL min^{-1} in a flow reactor. Samples were heated at 6 °C min^{-1} from 25 to 800 °C. Before TPR experiments, all the samples were stabilized with N_2 at room temperature for 1 h.

XPS determinations were carried out in a Multitechnic Specs photoemission electron spectrometer, equipped with an X-ray source Mg/Al and a hemispherical analyzer PHOIBOS 150 in the fixed analyzer transmission mode (FAT), operating with an energy power of 100 eV. The pressure of the analysis chamber was kept at pressure lower than 5.10^{-8} mbar. Samples prepared by RLP were only degassed in-situ while samples prepared by CI (previously reduced under H_2 at 350 °C for 3 h), were introduced in the equipment and additionally reduced "in-situ" with H_2 at 350 °C for 30 min. Peak areas and BE values were estimated by fitting the curves with combination of Lorentzian–Gaussian curves of variable proportion using the CasaXPS Peakfit software version 1.2. The binding energy values (BE) of the energy levels of the corresponding atoms species were referenced to the C 1s binding energy of 284.6 eV. Pt 4f spectra were deconvoluted as it was described elsewhere [31]. In the case of the samples with promoter metals several spectral regions (Fe 2p, Sn 3d, Ga 2p, Ga 3d, In 3d, and In Auger signals), both in samples with and without

previous reduction, were analyzed in order to ensure the correct fit between oxidized and reduced species [32, 33].

TEM measurements were carried out on a JEOL 100CX microscope with a nominal resolution of 0.6 nm, operated with an acceleration voltage of 100 kV, and magnification ranges of ×80000–×100000. For each catalyst, a very important number of Pt particles (about 200–300) were observed and the distribution curves of particle sizes were done. The mean metallic particle diameter (d) was calculated as: $d = \sum ni.di / \sum ni$, where n_i is the number of particles of diameter d_i.

3 Results and Discussion

3.1 Characterization of the Metallic Phase

3.1.1 TPR Profiles

Figure 1 shows the TPR profiles for the bimetallic catalysts supported on CNP and prepared by CI and RLP methods. For the sake of comparison, TPR profiles of the monometallic catalyst, support and samples of each promoter prepared by CI are also included. It can be observed in Fig. 1 that the CNP support displays one broad H_2 consumption zone at temperatures higher than 400 °C related both to the decomposition of weaker acid functional groups of the support that desorb CO and the simultaneous creation of unsaturated reactive surface sites that interact with hydrogen at high temperatures [27, 28, 34, 35].

TPR profiles of each promoter also show an H_2 consumption zone at high temperatures. Fe (2.5 wt%)/CNP–CI sample displays two H_2 consumption zones: the first one showing a broad peak (350–700 °C) corresponding to the reduction of ionic Fe [27, 36–38] and a shoulder (625–675 °C) coincident with the maximun of the consumption zone of the support. For Sn(3 wt%)/CNP–CI, the reduction profile begins at about 200 °C with a small intensity which is notoriously increased until overlapping with the H_2 consumption zone of the support at high temperature [27]. In the case of Ga sample, there is a broad reduction zone above 300 °C, however it seems to exhibit an inhibition (total o partial) in the H_2 consumption at high temperature from functional groups of the support [27]. The In profile was similar to the Sn one begining at 250–300 °C with two or three peaks between 300 and 750 °C, the latter ones overlapping with the one of the support [27].

The TPR profile of the Pt/CN–CI shows a reduction peak with a maximum at about 180–200 °C that would correspond to the reduction of the deposited Pt metallic complex to zerovalent state [26, 36, 37, 39]. There also are H_2 consumption zones at temperatures higher than 250 °C due to additional effects produced both by the presence of Pt

Fig. 1 TPR profiles for the bimetallic catalytic series prepared by CI and RLP: **a** PtFe, **b** PtSn, **c** PtGa and **d** PtIn
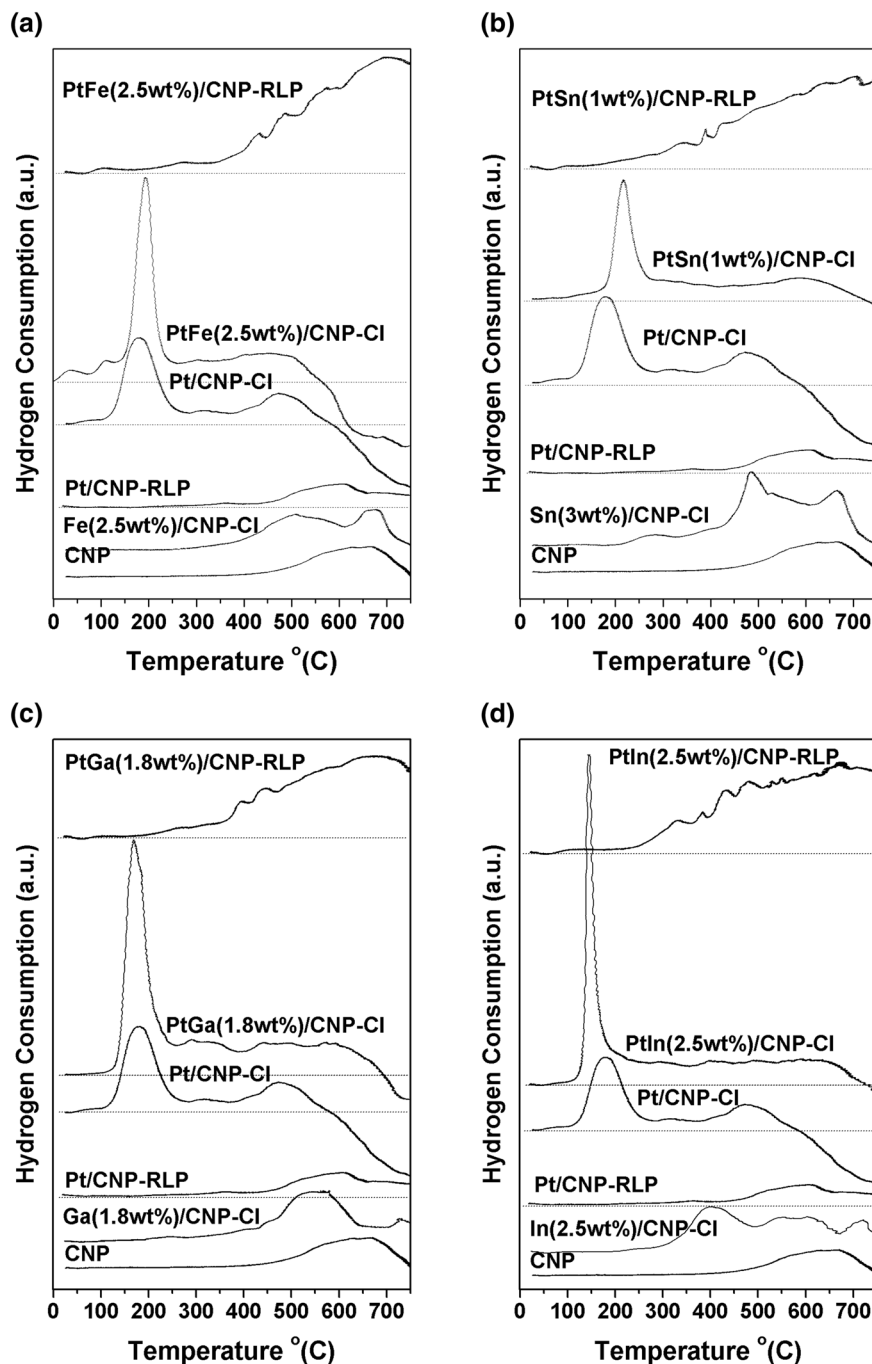
and the thermal treatment with hydrogen during the TPR test [34, 35, 40]. In this sense, the H_2 consumption zone at high temperatures observed in the TPR profile of the support is shifted to lower temperatures in the monometallic catalyst since Pt particles would produce a catalytic effect on the decomposition of the functional groups of the support.

The TPR profiles of the bimetallic catalyst series prepared by CI (see Fig. 1) show an important reduction peak between 100 and 250 °C (in the Pt reduction zone of the monometallic catalyst), additional peaks or H_2 consumption zones above 250 °C and in some cases, a desorption zone at temperatures higher than 550 °C. Pt reduction peak in bimetallic samples is shifted to higher or lower temperatures, with respect to the monometallic catalyst, depending on the promoter, except for the PtFe/CNP–CI sample. Hence, in PtGa and PtIn catalysts, there would be different Pt species than in PtSn and PtFe ones, which would be more reducible in bimetallic catalysts than in the monometallic one.Other difference between

mono and bimetallic catalysts prepared by CI indicates that all the peaks of the bimetallic samples at low temperatures show higher intensity than that corresponding to the monometallic one, as it can be deduced from the comparison of the corresponding profiles and also from the measurements of the consumed H_2 amounts taken into account the value theoretically expected from the reduction of all platinum from Pt(IV) to Pt(0) when the Pt content is 5 wt%. In conclusion, these effect would be indicating the Pt reduction and a simultaneous catalytic reduction effect of the Pt on the promoter.

Regarding the profiles at high temperature for CI-prepared bimetallic samples, it must be noted that the TPR profile of PtFe sample shows one small and broad peak at temperatures higher than 400 °C and an intermediate reduction zone between this peak and the Pt reduction one. The intermediate zone could be due to a catalytic reduction effect of the Pt on a Fe fraction, which would be present in the vicinity of the Pt. The reduction zone at higher temperatures is coincident with the Fe reduction zone, thus indicating that an important fraction of Fe could remain as ionic species stabilized on the support after the catalyst reduction, similarly as it happens for the PtGa sample. The contrary occurs for PtSn and PtIn samples, where the TPR profiles would be evidencing an important co-reduction of the metals (Pt and Sn or In) and that the amount of free promoter species on the supports would be significantly lower than for PtFe or PtGa samples. Besides, in the PtSn and PtIn catalysts, the hydrogen retention over the carbon surface is lower, since in these samples neither an important reduction of functional groups nor a significant desorption zone at high temperatures is observed as it happens for PtFe and PtGa catalysts. It seems that the hydrogen dissociated by Pt and spilt over the carbon surface is mainly used to reduce Sn or In promoter salts. These results would suggest that the promoters (Sn or In) reduced to the zerovalent state could be present in the Pt metallic phase opening the possibility to the formation of alloys with Pt.

Figure 1 also displays the TPR profile of the monometallic catalyst prepared by RLP, this showing no H_2 consumption at low temperatures in the Pt reduction zone of conventionally impregnated samples, so Pt is reduced in this catalyst during the preparation. Besides, this profile shows a H_2 consumption zone at temperatures higher than 300 °C, quite similar to that corresponding to the support (although with a lower H_2 consumption), but different from that corresponding to the Pt monometallic-CI sample. This would indicate not only a lower decomposition of functional groups of the support and simultaneous H_2 consumption by unsaturated reactive sites exposed after this decomposition, but also a lower catalytic effect on these phenomena and a lower retention of the hydrogen spilt over carbon surface as well.

Besides, it can be observed that all the profiles of the bimetalic RLP catalysts show a broad and more defined reduction peak in the zone where each promoter is reduced indicating that an important fraction of promoter could remain as ionic species stabilized on the support after reduction in liquid phase. These samples also show a small reduction zone at temperatures higher than 200 °C, which would be indicating a catalytic effect of the reduced Pt on the reduction of a small fraction of promoter. However, RLP method is performed at lower temperature than the temperature in which is observed this effect. In conclusion, unlike for catalysts prepared by CI, the TPR results suggest that in catalysts prepared by RLP a poor interaction between the metals would exist.

3.1.2 Test Reactions of the Metallic Phase

Cyclohexane dehydrogenation (CHD) and the benzene hydrogenation (BH), were used as tests of the metallic phase to indirectly measure the amount of exposed surface Pt atoms and evaluate the activation energy of these reactions. CHD was used to test catalysts prepared by CI and BH for RLP ones. CHD is a structure insensitive reaction carried out on the surface of active atoms and involving only one metallic Pt exposed site [41]. Catalysts prepared by CI were reduced at high temperature, but since RLP ones were reduced at low temperature, the BH test reaction was used for these catalysts because it is the inverse of the CHD reaction and it can be carried out al low temperatures [42, 43]. For catalysts prepared by CI, the cyclopentane hydrogenolysis (CPH), was also carried out. This is a structure-sensitive reaction taking place on ensembles of a certain number of active atoms, a change in the reaction rate can be observed if a modification of the metallic phase is produced by some geometric or electronic effect (breaking or reduction the metallic ensembles) [44]. Table 2 shows the results corresponding to initial reaction rate (R^0_{CH}) and activation energy (Ea_{CH}) values measured in the cyclohexane dehydrogenation, and initial reaction rate values measured in the cyclopentane hydrogenolysis (R^0_{CP}), for catalysts prepared by CI. Table 3 shows the catalytic behaviour (initial reaction rate, R^0_B, and activation energy, Ea_B) of samples prepared by RLP for the benzene hydrogenation reaction.

From results in Table 2, it can be observed that the R^o_{CH}, R^o_{CP} and Ea_{CH} values for catalysts prepared by CI are modified in different degree according to the nature of the promoter. Firstly, for PtSn catalyst whitout N_2 treatment it can be seen that both CHD and CPH initial reaction rates and Ea_{CH} are highly modified respect to the monometallic catalyst, indicating a strong electronic interaction between both metals and an important modification of the metallic phase with probable alloy formation, as well as a dilution

Table 2 Initial reaction rates of CHD (R^0_{CH}) and CPH (R^0_{CP}), and activation energy in CHD (Ea_{CH}) for the Pt–promoter catalyst series prepared by CI

Catalyst	R^0_{CH} (mol h^{-1} g^{-1} Pt)	Ea_{CH} (kcal mol^{-1})	R^0_{CP} (mol h^{-1} g^{-1} Pt)
Pt/CNP–CI	1.78	41	8.87
PtFe/CNP–CI	0.85	43	4.92
[PtFe/CNP]–N$_2$–CI	0.28	46	0.72
PtSn/CNP–CI	0.74	49	0.77
[PtSn/CNP]–N$_2$–CI	<0.05	n.m	0.28
PtGa/CNP–CI	0.22	37	0.09
[PtGa/CNP]–N$_2$–CI	<0.05	n.m	0.08
PtIn/CNP–CI	0.82	38	0.07
[PtIn/CNP]–N$_2$–CI	<0.05	n.m	0.06

CHD reaction conditions T = 250, 240, 230 °C, H$_2$/CH = 26.5; CPH reaction conditions T = 350 °C, H$_2$/CP = 23.1

n.m not measurable

Table 3 Initial reaction rates (R^0_B) and activacion energy (Ea_B) of BH for the Pt–promoter catalyst series prepared by RLP

Catalyst	R^0_B (mol h^{-1} g^{-1} Pt)	Ea_B (kcal mol^{-1})
Pt/CNP–RLP	1.85	13
PtFe/CNP–RLP	0.10	15
[PtFe/CNP]–N$_2$–RLP	<0.05	n.m
PtSn/CNP–RLP	0.77	14
[PtSn/CNP]–N$_2$–RLP	<0.05	n.m
PtGa/CNP–RLP	2.43	12
[PtGa/CNP]–N$_2$–RLP	0.90	11
PtIn/CNP–RLP	1.41	13
[PtIn/CNP]–N$_2$–RLP	<0.05	n.m

BH reaction conditions T = 110, 100, 90 °C, H$_2$/CH = 21.8

n.m not measurable

and/or blocking effects of Sn on Pt particles. Fe addition to Pt shows that both the CHD and CPH initial reaction rates decrease in an important degree (about 50%) in the PtFe bimetallic catalyst without N$_2$ treatment with respect to the monometallic one. However, the Ea_{CH} value in this catalyst is almost not modified with respect to the monometallic sample, so a poor electronic modification of the Pt by Fe together with an important geometric modification of the metallic phase by dilution or blocking of the surface Pt atoms is expected.Ga and In additions to Pt in catalysts untreated with nitrogen decrease the CHD reaction rate respect to the corresponding monometallic sample. For both cases, Ea_{CH} values are slightly lower than the monometallic catalyst, these behaviours were observed in previous studies [45]. In these catalysts there could exist an important interaction between Pt and Ga or Pt and In with

probable formation of a fraction of alloyed species. However, contrary to PtSn alloyed species above mentioned, these PtGa and PtIn species could be more active than the Pt active sites in CHD, as it can be deduced from a promotion of the dehydrogenation in active sites with a minor activation energy [45]. In this sense, the results agree with TPR experiments, that indicated an important co-reduction Pt–promoter, and that PtGa and PtIn species would have different electronic properties and be more reducible than those of Pt or the ones PtSn or PtFe systems. Besides, for PtGa and PtIn catalysts, R^0_{CP} values significantly decrease with respect to the monometallic sample so these promoters break almost all the necessary ensembles for the hydrogenolysis reaction and induce an important geometric effect by dilution or blocking of the Pt surface atoms.

Table 2 also shows the test reaction results for CI catalysts treated with N$_2$. In these cases, it must be noted that both the possible modification of particles sizes towards larger ones (sinterization) and the formation of a new arrangement of the metallic phase due to the thermal treatment with N$_2$, would decrease the final fraction of exposed Pt atoms. Indeed, these series showed very lower, almost negligible, initial reaction rates for both reactions than for untreated catalysts, this indicating that even though the strong interaction Pt–promoter remains, there would be a different modification of the metallic phase.

Table 3 shows the results of RLP catalysts in the benzene hidrogenation. In general, in bimetallic catalysts untreated with nitrogen, the addition of a second metal to Pt decreases the R^o_B according to the nature of the promoter, but without a significant change in the activation energy (Ea_B). In these sense, it must be noted that R^0_B decreases in different degree in PtFe, PtSn and PtIn bimetallic catalysts with respect to the monometallic one, this decreasing being very significant for PtFe couple. On the contrary, the PtGa catalyst shows an activity value higher than the monometallic one and the Ea_B value slightly decreases with respect to the monometallic sample, these behaviors being similar to that found in the CHD reaction for the same bimetallic sample prepared by CI. Thus, except for the PtGa sample, the non-significant modification of Ea_B and the decrease in the initial activity in the PtFe, PtSn and PtIn bimetallic couples prepared by RLP, indicate a poor or null electronic modification of Pt by Fe, Sn, or In, and only geometric effects in the metallic phase would be present in these catalysts. It should be noticed that the type of geometric modification (dilution or blocking effects, aggregates, islands, decoration of Pt by the second metal, core–shell type particle morphologies, etc.) of the metallic phase of RLP catalysts cannot be deduced from this test reaction. However, promoter species intercalated in the metallic phase can act as Lewis acid sites and enhance the polarization of the carbonyl group enabling it to react with hydrogen dissociated

on the Pt atoms, this effect taking place if the promoter species are placed in the vicinity of the Pt atoms. Hence, it can be deduced that the higher the amount of promoter atoms in the vicinity of Pt ones, the higher the promotion of the carbonyl group, and in consequence, the most ordered arrays of uniform ensembles with the lowest amount of blocked Pt atoms would correspond to the catalytic phase with the best performance.

Table 3 also shows the results of BH for catalysts prepared by RLP and treated with nitrogen. The initial reaction rate (R^0_B) sharply decreases in all the samples and it is almost negligible. These results would indicate a higher geometric modification than that observed for the parent untreated catalysts, this behaviour being similar to that observed for CI catalysts treated with nitrogen in CHD test reaction.

Summarizing the results of test reaction of catalysts prepared by both methods treated and untreated with nitrogen, it can be concluded that the bimetallic phases are very different. Bimetallic catalysts prepared by CI show evidences of strong geometric and electronic modifications of the Pt metallic phase by the second metal, whereas in catalysts prepared by RLP, only a geometric modification of the bimetallic phases exists, which seems to be different from that found in catalysts prepared by CI and very dependent on the nature of the second metal and the nitrogen thermal treatment.

3.1.3 XPS Measurements

XPS spectra corresponding to Pt 4f, Fe 2p, Sn 3d, Ga 2p or 3d, In 3d, C 1s and O 1s core levels of the mono and bimetallic catalysts prepared by CI and RLP were determined. Figure 2 shows the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ XPS spectra for monometallic catalysts prepared by CI and RLP. Figure 3 shows some selected XPS spectra for Fe 2p, Sn 3d, Ga 2p or 3d, and In three-dimensional regions of the all the bimetallic catalysts prepared by both methods. For the sake of comparison XPS spectra of different core levels corresponding to the monometallic samples of the different promoters prepared by CI and RLP are also included. Tables 4 and 5 compile Pt $4f_{7/2}$, Fe $2p_{3/2}$, Sn $3d_{5/2}$, Ga 3d, and In $3d_{5/2}$ XPS binding energies (BE), percentajes of the species with different oxidation states, and the Pt_T/C and P_T/Pt surface molar ratios (Pt_T and P_T: total moles of Pt and promoter respectively) of the catalytic series prepared by both methods.

From XPS spectra displayed in Fig. 2, it can be observed that the Pt 4f spectra of the monometallic catalysts show an asymmetry at about 76–80 eV since a certain amount of ionic species of Pt(II) or Pt(IV) masks the main signal from Pt^0 at about 71–72 eV [28]. Ionic Pt forms oxides species with specific groups of the support which remains unreduced at the temperature used to obtain the final catalyst [28]. From the deconvolution of Pt 4f XPS spectra, three doublets were obtained: (i) one at about 71.5–72.0 eV for Pt $4f_{7/2}$ and the corresponding values for Pt $4f_{5/2}$ shifted at 3.35 eV for Pt^0; (ii) other at 72.8–74.0 eV for Pt $4f_{7/2}$ and the corresponding values for Pt $4f_{5/2}$ shifted at 3.35 eV at higher BE, assigned to Pt(II) species; and (iii) a third one at 75.1–77.6 eV for the Pt $4f_{7/2}$ and the corresponding values for Pt $4f_{5/2}$ shifted at 3.35 eV at higher BE, assigned to Pt(IV) species.

Fig. 2 XPS profiles of Pt for the monometallic catalysts prepared by: **a** CI and **b** RLP
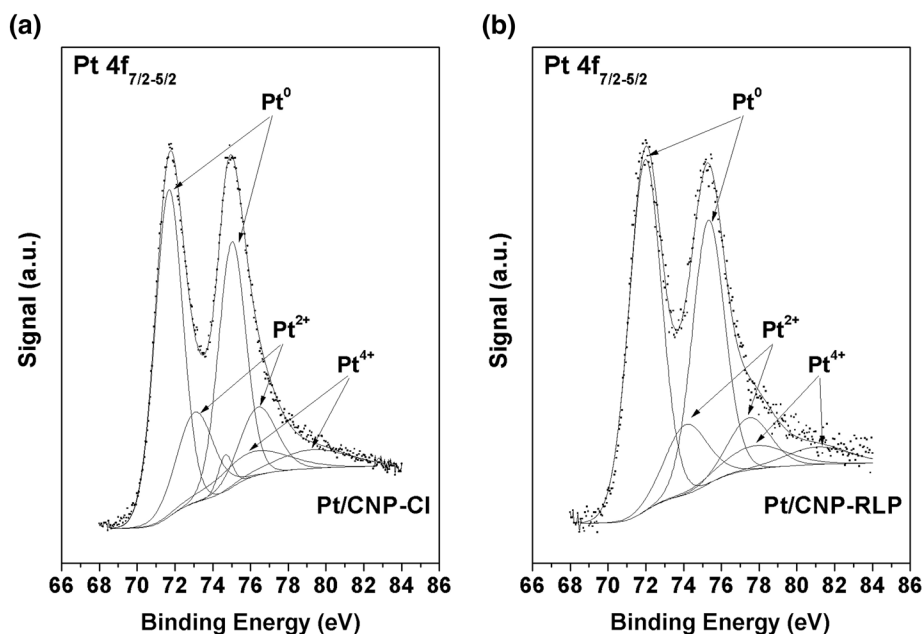
Fig. 3 XPS profiles of Pt–promoter catalysts prepared by CI and RLP: **a** Fe level, **b** Sn level, **c** Ga level and **d** In level
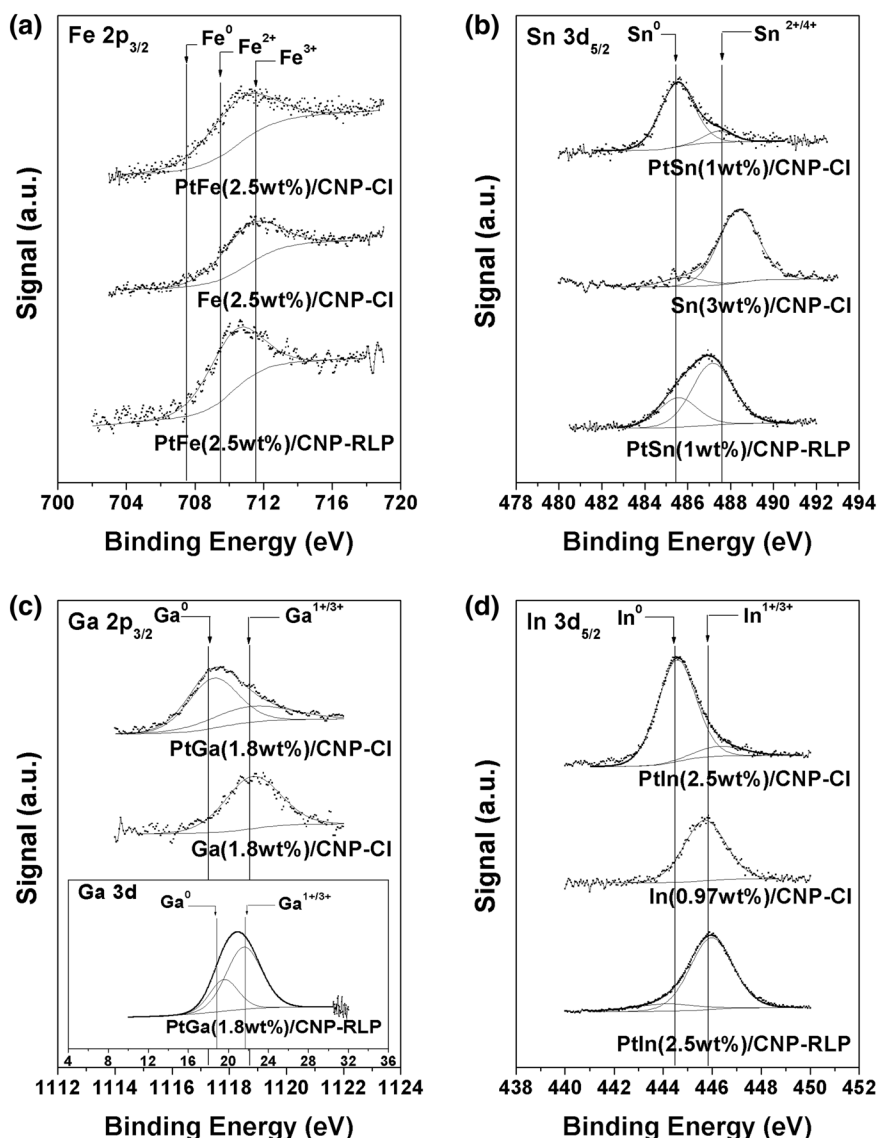
Table 4 XPS results of the Pt–promoter catalyst series prepared by CI

Catalyst	Atomic ratio		Pt 4f$_{7/2}$ level			Fe 2p$_{3/2}$, Sn 3d$_{5/2}$, Ga 2p or In 3d$_{5/2}$ level		
	Pt/C	P/Pt	BE (eV)	Species	%	BE (eV)	Species	%
Pt/CNP–CI	0.60	–	71.67	Pt^o	63.60	–	–	–
			73.06	Pt^{+2}	23.60			
			75.95	Pt^{+4}	12.80			
PtFe/CNP–CI	0.57	0.76	71.83	Pt^o	68.20	710.54	Fe$^{+2/+3}$	100.00
			73.47	Pt^{+2}	20.40			
			76.55	Pt^{+4}	11.40			
PtSn/CNP–CI	0.56	1.57	72.05	Pt^o	82.40	485.52	Sn^o	87.10
			73.44	Pt^{+2}	8.50	487.45	Sn$^{+2/+4}$	12.90
			75.10	Pt^{+4}	9.30			
PtGa/CNP–CI	0.38	4.67	71.93	Pt^o	79.00	1117.04	Ga^o	65.90
			73.50	Pt^{+2}	10.80	1118.34	Ga$^{+1/+3}$	34.10
			75.11	Pt^{+4}	10.20			
PtIn/CNP–CI	0.45	1.07	71.60	Pt^o	79.80	444.26	In^o	89.30
			73.26	Pt^{+2}	11.10	446.02	In$^{+1/+3}$	10.70
			75.49	Pt^{+4}	9.10			

Table 5 XPS results of the Pt–promoter catalyst series prepared by RLP

Catalyst	Atomic ratio		Pt 4f$_{7/2}$ level			Fe 2p$_{3/2}$, Sn 3d$_{5/2}$, Ga 3d or In 3d$_{5/2}$ level		
	Pt/C	P/Pt	BE (eV)	Species	%	BE (eV)	Species	%
Pt/CNP–RLP	0.42	–	71.87	Pt^{o}	72.10	–	–	–
			74.03	Pt^{+2}	18.60			
			77.66	Pt^{+4}	9.30			
PtFe/CNP–RLP	0.19	1.21	71.65	Pt^{o}	71.60	710.54	Fe$^{+2/+3}$	100.00
			73.41	Pt^{+2}	18.70			
			77.20	Pt^{+4}	9.70			
PtSn/CNP–RLP	0.27	1.72	71.51	Pt^{o}	74.80	485.25	Sn^{o}	17.70
			72.83	Pt^{+2}	18.60	486.98	Sn$^{+2/+4}$	82.30
			75.54	Pt^{+4}	15.60			
PtGa/CNP–RLP	0.35	5.78	71.85	Pt^{o}	74.20	19.11	Ga^{o}	28.90
			73.70	Pt^{+2}	16.60	21.11	Ga$^{+1/+3}$	71.10
			75.31	Pt^{+4}	9.20			
PtIn/CNP–RLP	0.30	2.92	71.57	Pt^{o}	71.90	444.12	In^{o}	12.60
			73.35	Pt^{+2}	14.35	445.97	In$^{+1/+3}$	87.40
			75.94	Pt^{+4}	13.74			

Tables 4 and 5 show that the percentages of Pt(0) found for the monometallic catalysts prepared by both methods are between 60 and 75%. These results agree with those reported in the literature for catalysts supported on CN [27, 28, 46, 47]. Monometallic catalyst prepared by RLP shows a higher reduction degree than the monometallic one prepared by CI because after of the deposition of the Pt during the reduction step of the RLP preparation method two phenomena could occur: (i) an ionic exchange between Pt species anchored on the support and sodium from the solution, and (ii) the reduction of some surface oxygenated groups leaving free Pt species which would be more easily reduced.

The XPS results for the bimetallic catalysts prepared by CI reveal that the addition of a second metal increases the reducibility of Pt, this being more significant in catalyts with Sn, Ga, or In. In the homologous catalysts prepared by RLP, it is not observed an important change in the Pt(0) percentages after the addition of the second metal. During CI and drying steps, Pt would be reduced from Pt^{+4} (from the metallic precursor) to Pt^{+2} species by specific surface groups over carbon nanotubes [25, 28, 34, 35, 40, 48, 49], or by precursor species used as a promoter [49–51]. These Pt^{+2} species could then be more easily reduced to Pt^{0} than Pt^{+4} [25, 28]. In this sense Fe, Ga, and In precursors, which have the highest oxidation state, could suffer a previous redox reaction involving the reduction of these species by the support, as occurs with the Pt. Then these reactions could be coupled with the reduction of Pt^{+4} to Pt^{+2}. In the case of PtSn bimetallic catalysts the reduction of Pt precursor to Pt^{+2} by a redox process with Sn occurs directly, since the Sn has the lowest oxidation state in the precursor [34, 50, 51]. Thus, the fraction of Pt partially reduced by the second metal species, could contribute to the higher percentage of metallic Pt found in CI-prepared bimetallic catalysts. In the case of RLP catalysts, promoter and Pt species could be desorbed from the support to the reductor medium after the impregnation step of the RLP method so some of the redox reaction above mentioned would not occur. Besides, as catalysts prepared by RLP are dried after the reduction step, this fact could also explain the difference of Pt reducibility found in both methods.

Regarding the oxidation state of the promoters, the percentages of oxidized and reduced species corresponding to the bimetallic catalysts prepared by both methods are inverted (except for the PtFe catalyst) as it can be deduced from P(0)/P(ox) ratios (P: promoter) and the percentages of the species. In this sense, it is important to point out that for PtSn, PtIn and PtGa catalysts prepared by CI, the main fraction corresponds to reduced species. Besides, PtSn and PtIn catalysts showed a very high P(0):P(ox) ratio of about 90:10. These differences can be observed in Fig. 3. These results would indicate the formation of very different bimetallic phases according to the preparation method. In this sense, RLP does not allow neither the reduction of the second metal nor an important co-reduction between Pt with these promoters but CI method seems to be more effective to form alloyed phases, since according to test reaction results, the reduced promoter would be electronically modifying the Pt metallic phase.

The Pt/C surface molar ratio is rather constant for all the CI series, except for Ga, whose ratio is slighly decreases. For RLP series, these values are lower than the CI series and decrease respect to the monometallic sample. However, independently of either the metal or the preparation method no correlation can be deduced, it can only be postulated that Pt active metallic phase is modified by the second metal. A similar behaviour is found for the P/Pt surface molar ratio,

the ratios of the RLP series being higher than for the CI one. An exception is the PtGa couple showing the highest values of both series. Even though the values for nitrogen-treated catalysts were not showed in the table, the behaviours were similar and similar conclusions can be drawn, except for PtIn sample, since for this catalyst P/Pt showed a lower ratio than their parent catalyst without thermal treatment. Thus, these results show a certain surface enrichment (with Sn, In and Ga promoters), more pronounced for the PtGa couple and reveal different bimetallic phases according to the nature of the promoter, the preparation method and the N_2 thermal treatment.

3.1.4 TEM Measurements

TEM microphotographies were taken for some selected catalysts, prepared by both methods, together with those corresponding homologous catalysts submited to the thermal treatment with N_2. From these microphotographies, the corresponding histograms of particle size distribution were represented and the mean particle size was calculated. TEM microphotographies together with the corresponding histograms of particle size distribution of these catalysts are shown in Figs. 4, 5 and 6. Besides, the corresponding values of the mean sizes are summarized in Tables 6 and 7.

From results displayed in Figs. 4 and 5, it can be observed that both monometallic and bimetallic catalysts prepared by CI and without N_2 thermal treatment, show similar values of mean particle size so the addition of a second metal to the Pt metallic phase does not change the average particle size, as expected. However, histograms of particle sizes of the bimetallic catalysts seem to be narrower than those corresponding to monometallic catalysts, these results being in agreement with other works [52, 53]. For thermally-treated catalysts, the particle sizes slightly
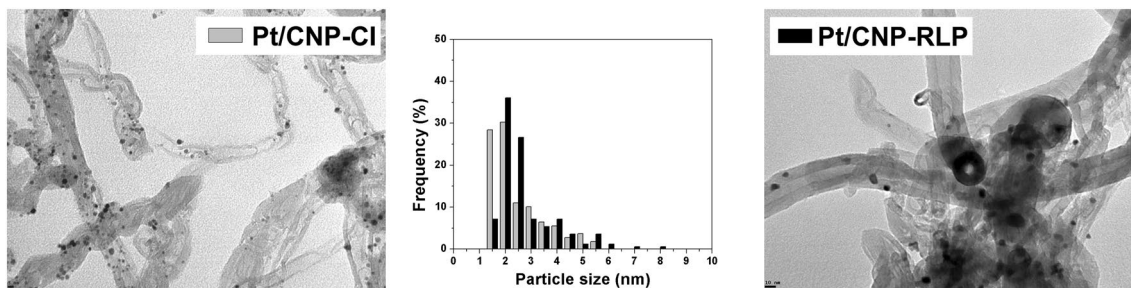

Fig. 4 TEM images and their distributions of particle diameters for Pt catalysts prepared by CI and RLP
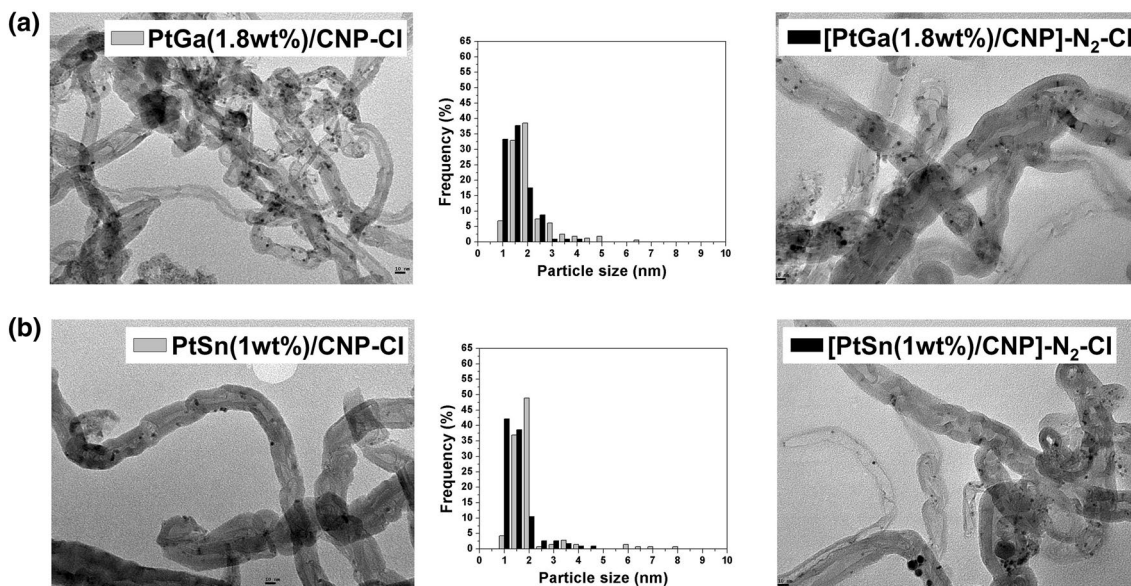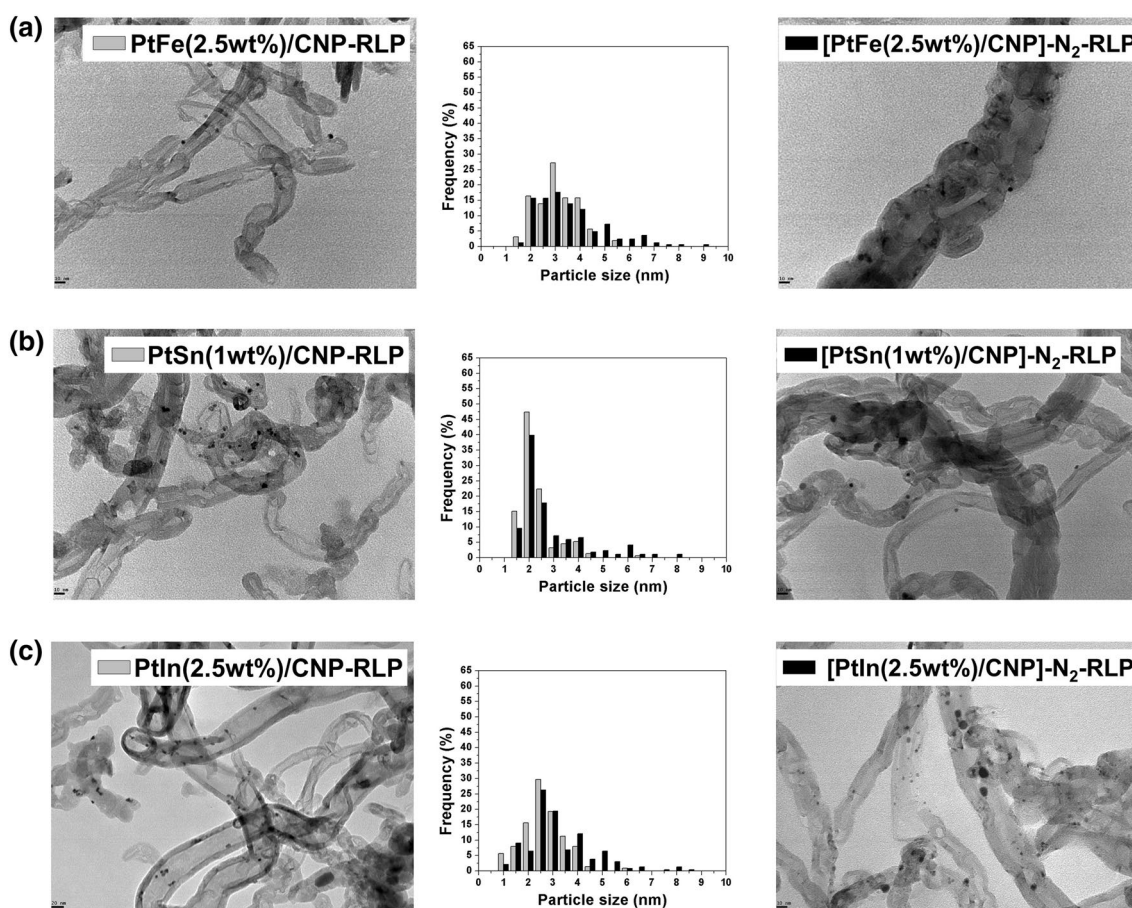

Fig. 5 TEM images and their distributions of particle diameters for bimetallic catalysts prepared by CI: **a** PtSn/CNP–CI and [PtSn/CNP]–N_2–CI, **b** PtGa/CNP–CI and [PtGa/CNP]–N_2–CI

Fig. 6 TEM images and their distributions of particle diameters for bimetallic catalysts prepared by RLP: **a** PtFe/CNP–RLP and [PtFe/CNP]–N$_2$–RLP, **b** PtSn/CNP-RLP and [PtSn/CNP]–N$_2$–RLP, **c** PtIn/CNP–RLP and [PtIn/CNP]–N$_2$–RLP

Table 6 Particle sizes determined by TEM of the catalysts prepared by CI

Catalyst	Mean particle size (nm)
Pt/CNP–CI	2.25
PtFe/CNP–CI	2.20
[PtFe/CNP]–N$_2$–CI	1.61
PtSn/CNP-CI	2.23
[PtSn/CNP]–N$_2$–CI	1.81
PtGa/CNP–CI	2.29
[PtGa/CNP]–N$_2$–CI	1.85
PtIn/CNP–CI	2.13
[PtIn/CNP]–N$_2$–CI	1.72

decrease with respect to their homologous without thermal treatment.

In a previous work [28] that agreed with other ones [54–57] it was reported that thermally-treated monometallic catalysts have larger particle sizes that favour the hydrogenation of the carbonyl group. For bimetallic catalysts this information is scarce or null. However, according to the results of this study with bimetallic catalysts, it can be suggested that the addition of a second metal would prevent the sintering of the metallic particles during the thermal treatment. The sintering resistance in supported metallic catalysts is related to the interaction between the metallic phase and the support surface (metal-support strength). It must be mentioned that the platinum precursor interaction could take place on two sites on the support: (i) oxygen surface groups, and (ii) π-complex structures on the carbon basal planes. It is the first interaction that could explain the beneficial effect on the platinum dispersion on activated carbons [25, 57], while the π-complex structures on the carbon basal planes, can be considered on graphitized carbons with a low oxidation degree like the carbon nanotubes [58, 59]. On the other hand, the higher the amount of oxygenated groups, the higher the hydrophilicity of carbon surface and the amount of water that could be retained on the carbon structure [57]. Besides, the interaction between platinum species and π-complex structures

Table 7 Particle sizes determined by TEM of the catalysts prepared by RLP

Catalyst	Mean particle size (nm)
Pt/CNP–RLP	2.96
PtFe/CNP–RLP	3.36
[PtFe/CNP]–N$_2$–RLP	3.75
PtSn/CNP–RLP	2.54
[PtSn/CNP]–N$_2$–RLP	3.10
PtGa/CNP–RLP	2.50
[PtGa/CNP]–N$_2$–RLP	4.40
PtIn/CNP–RLP	2.65
[PtIn/CNP]–N$_2$–RLP	3.22

is weakened by oxygen surface groups near π-sites, since they decrease the Lewis basicity due to an electron-withdrawing effect which destroys the electron deslocalization [60]. So, in the monometallic catalyst the metallic particles supported on a surface with a certain content of oxygenated groups [27, 28], could sinter under thermal treatment conditions in some proportion, since the presence of adsorbed water and the lower metal–support interaction in the π-sites near oxygenated groups would favour the migration of metallic species. Besides in this case the support would have a certain concentration of oxygenated groups not bonded to Pt which could be desorbed as CO and CO$_2$ leaving anchoring sites for metallic particles. The sintering resistance of bimetallic particles lies on the fraction of ionic species of the promoter that can be stabilized on the support and forming species with oxygenated acid groups of the carbon, thus inhibiting the desorption of these surface oxygenated groups caused by the temperature during the thermal treatment with N$_2$ and hindering the sintering and formation of larger particles.

In addition to the sintering resistence observed in bimetallic catalysts prepared by CI, the thermal treatment would produce other effect since the particle sizes of bimetallic catalysts are lower than their parent monometallic ones. According to the results corresponding to the histograms of particle size distribution displayed in Fig. 5 these catalysts have more uniform and similar particle size distributions ranging from 1 to 3 nm and with frequency percentages for particles with mean diameter of 1–1.5 nm higher than 70%, this showing an important contribution of small particles (not present in the non-thermally treated parent catalysts) to the total Pt area and thus, a higher dispersion. So, the thermal treatment would be producing a change in the particle morphology, being this change in the arrangements of the atoms due to the mobility of the promoters in the lattice crystal structure of Pt particles under the treatment condition. These physical changes could also induce a subdivision of the particles in order to produce bimetallic phases more stable with better interaction with the support. Besides, these new arrangements could involve both the alloyed phases and reduced promoter atoms, which could be segregated from the bulk to the surface of the particle. In relation to above suggestions, some effects or properties corresponding to bimetallic phases reported in the literature [61, 62] could help to clear out the final arrangements obtained in the bimetallic catalysts of this study. For example, it was reported that reduced Sn could be located both in the vicinity of the steps and on the terraces of the Pt particles depending on its concentration [61]. Besides, Sn, Ga, In atoms could form different chemical alloyed phases with Pt [32, 63]. A Pt-rich alloy such as Pt$_3$Sn was reported for samples prepared on oxidized carbon supports [62], thus evidencing that the amount of surface oxygenated groups on the support could influence the formation of different chemical phases.

Figure 6 displays TEM results corresponding to RLP catalysts. All the samples with and without thermal treatment show mean particle sizes higher than those found for CI-prepared ones. The addition of a second metal to the Pt metallic phase slightly changes the particle sizes (towards lower sizes, excep for PtFe sample). On the contrary, the thermal treatment increases the particle size. It is the preparation method that influences the particle size of catalysts since as it takes place in basic medium, it removes both the Pt and the promoter precursors anchored from the acid oxygenated groups of the support. Evidence of this fact was obtained when the support (i.e. without the addition of the metals) was treated with the basic solution (NaBH$_4$/ NaOH) following all the steps of the RLP method, the isoelectric point value of the support changed of 4.7–7.6, thus indicating that the groups acid were neutralized. Besides, as the reduction is carried out at low temperature, there is a higher percentage of Pt^0, as XPS indicates but the particles sizes are larger probably due to a different kinetic of platinum reduction and simultaneous aggregation of atoms to form particles during the addition of reducing agent [14, 64]. Besides, the increase in the particle size after the thermal treatment in all the catalysts prepared by RLP explains the sintering of RLP samples. The reduced particles could have a poor interaction with the support since the acid sites would be filled with other metals and the π-complex structures would be weakened by neighbouring oxygen surface groups during the preparation. These effects together the high availavily of free promoter species and the high hydrofilicity of the samples, could explain the slightly sintering observed in the catalysts prepared by RLP and treated with nitrogen.

Figures 5 and 6 show a high percentage of metallic particles corresponding to PtGa and PtIn catalysts prepared by both preparation methods which are placed inside the

carbon nanotubes channels. A higher percentage of bimetallic particles inside the channels was also observed in all the microphotographies taken for the PtGa and PtIn catalysts with respect to the corresponding to PtFe and PtSn catalysts. Thus, there would be a preferential distribution of the bimetalllic particles on the carbonaceous structure according to the nature of the promoter. Sn, Ga, In reduced species would form alloyed phases with Pt in catalysts prepared by CI. From TPR results it was observed a lower co-reduction temperature of the PtGa and PtIn species than those corresponding to the Pt, PtSn and PtFe catalysts and test reactions show a different electronic modification of the Pt phase by Ga and In promoters in comparison to the activities found for the other catalysts. PtSn, PtIn, PtGa, PtTl, PtSnTl, PtSnGa and PtSnIn alloyed phases on carbons were reported [33, 52, 65–67]. Results of charaterization in these studies indicate that a charge transfer from promoter to Pt occurs in agreement with the relative electronegativities of the atoms. On the other hand, it must be taken into account that the graphite layered-structure of the CN can lead to an electron-deficient inner surface and an electron-enriched outer surface [25, 38, 55, 68, 69]. These facts in relation to the support and alloyed phases can explain the deposition of PtGa and PtIn bimetallic particles inside the nanotubes channels. Because of this electronic modification, surface Pt atoms would be more negatively charged for the PtGa or PtIn alloys than for PtSn alloyed phases and pure Pt and probably PtGa and PtIn particles would be repelled from the external surface of carbon nanotubes, and hence confined inside the nanotube channels.
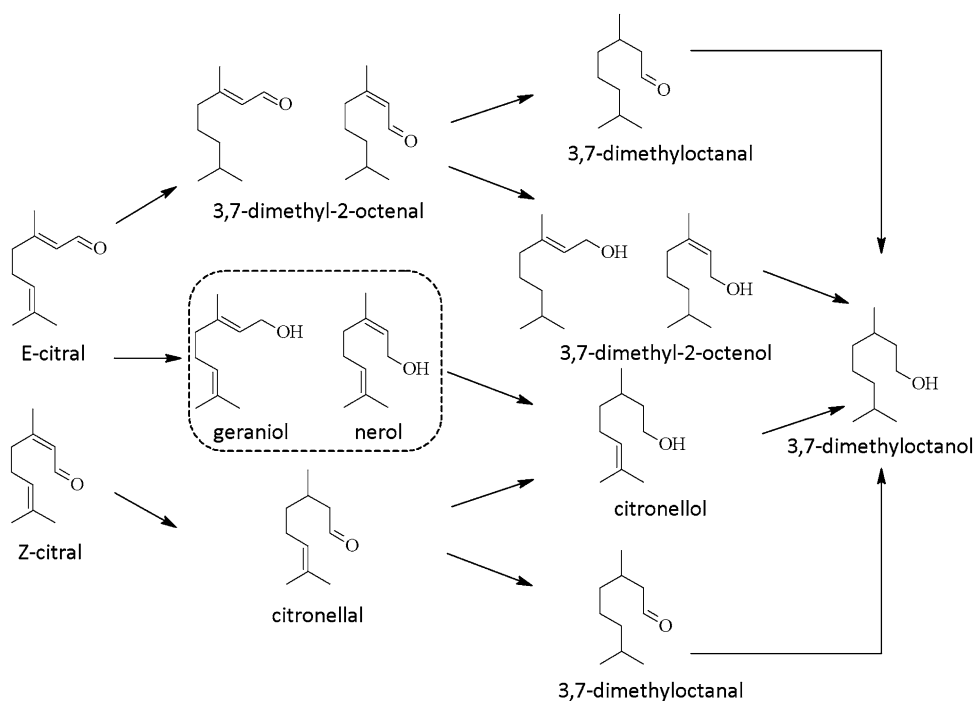
3.2 Citral Hydrogenation

Figure 7 shows the scheme of citral hydrogenation.The hydrogenation reaction of this substrate would proceed by any of the parallel and consecutive reduction routes shown in the scheme without a selective catalyst since the carbonyl group (C=O), double bond (C=C) conjugated with the carbonyl group, and the isolated double bond (C=C) of the citral can be hydrogenated. 2-propanol was selected as a solvent to avoid the formation of acetals. Other side reactions were negligible at these conditions [27, 70, 71].

Tables 8 and 9 show the results of citral hydrogenation for the two catalytic series prepared by different methods. For bimetallic catalysts prepared by CI, metal optimum loadings were selected according to previous works [27, 45], and similar loadings were used to prepare RLP catalyst series. It must be noted that for these selected loadings, the Promotor/Pt molar ratios depend on the nature of the promotor.

From results in Table 8, it is observed that all the bimetallic catalysts prepared by CI (with and without thermal treatment) display higher selectivities to UA than the monometallic ones as expected from the promoter role of the second metal. The selectivity to UA notoriously increase from a very low percentage about 7% for monometalic catalyst to above 89% [4–6]. This fact indicates that in bimetallic catalysts the hydrogenation of the carbonyl group is preferentially favoured respect to the hydrogenation of the double C=C bonds since different species of promotor (ionic, reduced or alloyed) can induce geometric and/

Fig. 7 The pathways of citral hydrogenation

Table 8 Results of citral hydrogenation for the catalysts prepared by CI: selectivity to UA (S_{UA}) and reaction time at 95% citral conversion

Catalyst	S_{UA} (%)	Time (h)
Pt/CNP–CI	7.20	7.00
PtFe/CNP–CI	92.70	7.50
[PtFe/CNP]–N$_2$–CI	95.20	20.00
PtSn/CNP–CI	89.20	3.00
[PtSn/CNP]–N$_2$–CI	96.70	7.00
PtGa/CNP–CI	90.70	0.75
[PtGa/CNP]–N$_2$–CI	98.00	12.00 (66%)[a]
PtIn/CNP–CI	97.00	0.40
[PtIn/CNP]–N$_2$–CI	94.50	0.13

[a]Values in brackets correspond to different citral conversion percentages than 95%

Citral hydrogenation reaction conditions: 0.3 mL of citral catalysed by 300 mg of the catalysts in 30 mL of 2-propanol, T = 70 °C, atmospheric pressure

Table 9 Results of citral hydrogenation for the catalysts prepared by RLP: selectivity to UA (S_{UA}) and reaction time at 95% citral conversion

Catalyst	S_{UA} (%)	Time (h)
Pt/CNP–RLP	16.20	3.50
PtFe/CNP–RLP	90.40	20.00
[PtFe/CNP]–N$_2$–RLP	88.70	8.00 (2%)[a]
PtSn/CNP–RLP	3.50	2.00
[PtSn/CNP]–N$_2$–RLP	79.00	12.00
PtGa/CNP–RLP	28.40	6.00
[PtGa/CNP]–N$_2$–RLP	75.90	3.50 (2%)[a]
PtIn/CNP–RLP	46.20	6.50
[PtIn/CNP]–N$_2$–RLP	n.m	n.m

[a]Values in brackets correspond to different citral conversion percentages than 95%

n.m not measurable, *citral hydrogenation reaction conditions* 0.3 mL of citral catalysed by 300 mg of the catalysts in 30 mL of 2-propanol, T = 70 °C, atmospheric pressure

or electronic effects in the active metallic phase to produce sites with a given surface structure acting as Lewis acid sites [5, 27]. Besides as selectivity values of thermally-treated CI catalysts (PtFe, PtSn ad PtGa samples) are higher than non-treated ones, changes in the metallic phase induced by this step would modify the metallic particle morphology improving the interaction metal-promoter [18, 27, 54–57, 68, 72, 73].

PtFe catalysts have a very high Promoter/Pt molar ratio (>>1), so Fe seems to be a less effective promoter than the other ones. In and Sn, seem to be the most efficient promoters since these catalysts showed relatively high selectiviy values to UA with low Promoter/Pt molar ratios (<<1). An effect that could affect the efficiency as a promoter, is

the fact that the Fe is a d-transition element and the other promoters are s,p ones, these characteristics affecting the behavior toward the hydrogenation of C=C and C=O groups, as it was mentioned in previous studies [5, 27, 36, 57].

All non-treated bimetallic catalysts show higher activities than the monometallic one, except the PtFe catalyst. It is knowed that the higher the promoter loading, the lower the activity [26, 27, 72, 74, 75], being in agreement when the metallic particle size does not change after the addition of the promoter. From our previous studies [27] it was shown that the activity become even lower than that corresponding to the monometallic catalyst only when very high promoter loadings were used. So, the highest activities of the bimetallic catalysts could be explained taken into account the relatively lower Promoter/Pt molar ratios used in PtSn, PtGa and PtIn samples. So, in absence of competitive hydrogenation and side reactions, and limitations to mass transfer, it is logic to consider an increase of the reaction rate.

Thermally-treated PtFe, PtSn and PtGa bimetallic catalysts show lower activities than their non-treated parent bimetallic catalysts, however PtIn catalyst without thermal treatment have very high activity that increases with the thermal treatment. Since, TEM results showed a lower particle size in all the catalysts treated with N$_2$, these facts would be more related to changes of the metallic phase morphology due to the thermal treatment than to the particle size.

For RLP catalyst series (see Table 9), except for the PtFe sample, the selectivities to UA in untreated bimetallic catalysts with N$_2$ are very lower than CI-parent samples. Besides, in spite of that thermally treated ones show higher selectivities to UA than non-thermally-treated ones, excepting for the PtFe catalyst no other catalyst without thermal treatment with N$_2$, reaches the selectivity to UA of its parent homologous prepared by CI. This behavior is different to that of the CI series. The monometallic catalyst gives better, but still low selectivity to UA, than the CI monometallic sample. These results are unexpected from the point of view of the role that a second metal added could have as a promoter. It was reported [21, 22] a good interaction between the active metals and the promoters in bimetallic catalysts prepared by RLP used in selective hydrogenation. In our case, a good interaction between Pt and the other promoters was not found, except for the PtFe sample. For this catalyst it is expected the modification of the metallic phase that promotes the hydrogenation of C=O group since Fe could form a complex under the preparation conditions and this fact would favour the deposition and interaction of both metals in the final catalyst [76, 77].

With regard to the activity of the catalysts prepared by RLP, non-thermally treated bimetallic catalysts except the

PtSn one, show lower activity than the parent catalysts prepared by CI (and also even lower than those corresponding to the monometallic catalyst), probably due to a competence between hydrogenation and other side reactions, the last ones being promoted by the RLP method [27, 28]. It must be taken into account that for RLP-method, the additon of a second metal would modify in a different way the metallic phase (and also the surface of the carbon) with respect to the catalysts prepared by CI. In the case of thermally-treated PtFe and PtIn catalysts the activity is significantly decreased or completely inhibited and for the PtGa couple, the thermal-treatment improves the selectivity to UA but the catalyst seems to be poisoned after a few reaction hours. PtSn catalysts lead to a very good selectivity but a low activity.

Relating the characterization results by test rections with those from hydrogenation, it can be deduced that all the bimetallic catalysts prepared by CI, whose metallic phases are diluted and Pt atom ensembles are broken but with the lowest amount of blocked Pt atoms, notoriusly improve the selectivity to UA in comparison to the monometallic catalyst. For bimetallic catalysts prepared by RLP, only the PtFe catalyst shows high selectivity to UA, thus evidencing that the geometric effect suggested by the sharp modification of BH initial rate involves a significant dilution of Pt atoms with a breakage of ensembles, in a similar way to that found for the same parent catalyst prepared by CI. As it was above mentioned, Fe could form complex and alloyed phases with Pt [6, 76–80] but as BH test indicates, no alloys are formed, so it is the complex that would induce the good Pt–Fe interaction and highly ordered arrays of the catalytic phase. On the other hand, even when the decrease of R^0_B in PtSn catalyst was significant, the very low selectivity to UA indicates a poor dilution and ensemble breaking effect of Pt by Sn, leading to aggregates of Sn species or Pt particles decorated or sprinkles by Sn ones. PtGa and PtIn catalysts prepared by RLP, show a moderate increase of the selectivity to UA in comparison to the monometallic one. These catalysts could have bimetallic phases geometrically modified with a higher dilution and breaking of the Pt atom ensembles and a lower blocking effect than PtSn catalysts.

Besides, activity changes observed in some thermally treated CI samples are more notorious than selectivity ones, the last effect not being very significant considering that the corresponding parent bimetallic catalysts without nitrogen treatment have a very high selectivity to UA. These small selectivity changes would be related to geometric changes in the metallic phase, such as a higher dilution (as test reactions indicate) changing the morphology of the Pt particles since, as the activity decreases in these catalysts, the metallic particle size decreases. On the contrary, in thermally-treated RLP samples, changes in activity and selectivity in the citral hydrogenation are very significant and dependent on the promoter. In general the RLP series has a lower activity than CI one, these decreasing even more when thermally treated. BH reaction results show that the metallic phases of all the catalysts prepared by RLP would be strongly modified by the thermal treatment, however, from citral hydrogenation results it is evident that different geometric effects would be present in comparison with those of CI method. The thermal treatment on PtSn–RLP catalyst, induces an adequate rearrangement of the bimetallic phase and/or the development of new sites mainly due to the dilution effect of the Pt atoms by Sn. Except for PtFe catalyst, whose selectivity to UA is not significantly affected, other couples prepared by RLP seem to suffer mainly a blocking effect of the Pt atoms in the metallic particles due to the termal treatment. It can be concluded that the higher the ordering of metals in the bimetallic phases as uniform ensembles, the higher the selectivity to UA. A highly ordered phase would have the highest amount of Lewis acid sites in intimate contact with Pt atoms where the carbonyl group of the α,β-unsaturated aldheyde is preferentially promoted towards its hydrogenation with respect to the unsaturated double bond.

Regarding XPS results and their relation with those of hidrogenation ones, different species of promotor (ionic or reduced) have been found. The best known promotion mechanism for the hidrogenation of carbonyl group is the one that involves ionic species of promoter acting as Lewis acid sites [5, 6, 78]. Even though XPS results show the presence of ionic species that would promote the hydrogenation of the carbonyl group in RLP catalysts, except for the PtFe sample, this effect is not very significant.The fact that the promotion mechanism with ionic species as Lewis sites is not highly effective for PtSn, PtGa and PtIn bimetallic catalysts prepared by RLP, would be related to a different modification of the metallic phase which would not correspond to homogeneously intercalated ionic species of the promoter in the Pt metallic phase as it was suggested by test reaction results. Besides, these modifications would indicate the presence of aggregates of the second metal on the Pt metallic phase, that would produce a blocking effect. On the other hand, CI samples show a high fraction of reduced species and give good selectivity to UA. In these cases, alloyed phases evidenced by TPR and test reactions analysis induce the high selectivity to UA [27, 45]. The PtSn, PtIn and PtGa alloys change the surface polarity, this improving the selectivity to UA. However, this mechanism would prevail only for PtIn and PtSn catalysts, since the concentration of ionic species in these catalysts is very low. In the case of the PtGa catalyst, which has appreciable amounts of reduced and ionic promotor species, both mechanisms could contribute to the promotion of the hydrogenation of carbonyl group. Besides, it must be noted

that the polarity of the PtIn alloyed surface would be higher than the PtSn one, since the selectivity to UA is higher for PtIn sample. PtSn–CI catalyst shows high selectivity to UA and it decreases the activity after the thermal treatment, so there could be a segregation of Sn and ordered alloys with higher coordination of Sn atoms than before the thermal treatment. Moreover, PtIn–CI catalyst, gives lower selectivity to UA after the thermal treatment suggesting a lower amount of In surface atoms in the arrangements of the bimetallic phase.

In conclusion, it must be pointed out that the final arrangement of the atoms of the metallic phase before and after the thermal treatment for CI catalysts would be governed by different types of interactions (metal–metal and metal–support) and according to the nature of the promoter and the properties of the support used.

For the RLP series, the higher amount of Pt free species desorbed of the support would lead to a higher percentage of reduced Pt (see XPS results), but also a higher particle size probably due to uncontrolled reduction kinetics of Pt and a simultaneous aggregation of atoms during the addition of reducing agent [14, 64]. The slight increase in the Pt paticle size leads to a slightly higher selectivity to UA in the monometallic catalyst prepare by RLP than those prepared by CI. Besides, under the conditions of the RLP-method, the reducing agent would not be able to reduce efficiently the promoter metallic precursors to the metallic state, and also the reduced Pt would not catalyze the co-reduction of the promoter metals by activation of hydrogen as occur under the conditions of the CI-method. So, since the reducing agent is added in excess, the low fraction of reduced promoter species found in the RLP catalysts would be formed from oxidation–reduction reactions with the support. In these bimetallic samples prepared by RLP, the positive effect of larger particles than those found for the corresponding CI catalysts does not help to improve the selectivity to UA, since the bimetallic phases obtained by RLP would not be as suitable as those obtained by the CI-method, except for the PtFe catalyst. However, in the last case, it is probably that the difference in the selectivity values to UA reached for the PtFe catalysts prepared by both method is caused by different modifications of the support from basic medium that lead the RLP method, thus infering that side reactions could not be totally inhibited in catalysts prepared by RLP.

Considering N_2-treated and untreated catalyst series, the metallic phases seem to be more highly ordered for CI samples than RLP ones (except for the PtFe catalyst), that can form a complex with Pt during the RLP, showing a better selectivity to UA. For the other bimetallic catalysts prepared by RLP there is not an apparent evidence that indicates an interaction between Pt and promoter previous to the reduction step. In consequence, it must be considered that if a high fraction of Pt and promoter species would be free in solution or if would remain on the support but without interacting during the reduction step, it is unlikely that the ionic species of the promoters were trapped in the crystal lattice of the Pt particles to form regular bimetallic arragement. Besides, it is also unlikely that metals interact effectively during drying step. Besides, the low concentration of reduced Ga and In species in RLP samples leads to a low concentration of alloys that also explain a poor selectivity to UA.

RLP method induce high availability of free promoter species and high hydrofilicity of the samples, but also sintering in thermally-treated RLP samples. However, improvement in the selectivity to UA by the sintering of Pt particles is only seen in thermally-treated PtSn–RLP sample since the other ones would suffer a blocking effect of the promoter over Pt active sites during the thermal treatment. Only Sn conforms highly-ordered phases after thermal treatment, probably because its ions could find a stable place in the crystal lattice of reduced Pt particles. Nevertheless, ionic species would be thermodynamically more stable and in consequence it is more probably that only form islands on the particle surface. That is the reason the CI method is more effective to form geometrically diluted phases by the promoter than RLP one due to the simultaneous co-reduction of Pt–promoter that induces intimate contact between both metals. Thus, in conclusion all the characterization and the hydrogenation results agree and suggest the formation of a phase adequately modified by the promoter with regular arragement of the atoms in catalysts prepared by CI and a phase less homogeneous for catalysts prepared by RLP, excepting for PtFe catalysts.

Figure 8 shows a scheme of the proposed surface models of atom arrangements for catalysts prepared by both methods with and without N_2 thermal treatment, the first one representing highly ordered phases with mainly promoter ionic species (for example, those corresponding to the PtFe catalysts prepared on both methods), the second one representing highly ordered phases with mainly Pt–promoter alloyed species (for example, those corresponding to the PtSn and PtIn CI catalysts), and the third one representing scarce ordered phases with mainly promoter ionic species (for example, those corresponding to the Pt–promoter catalysts prepared by RLP, except PtFe catalyst and PtSn catalyst treated with N_2).

4 Conclusions

Hydrogenation results highly depend on the catalyst preparation method, the thermal treatment as well as the nature of the second metal added to Pt. All bimetallic catalysts prepared by CI present better activities and selectivities to
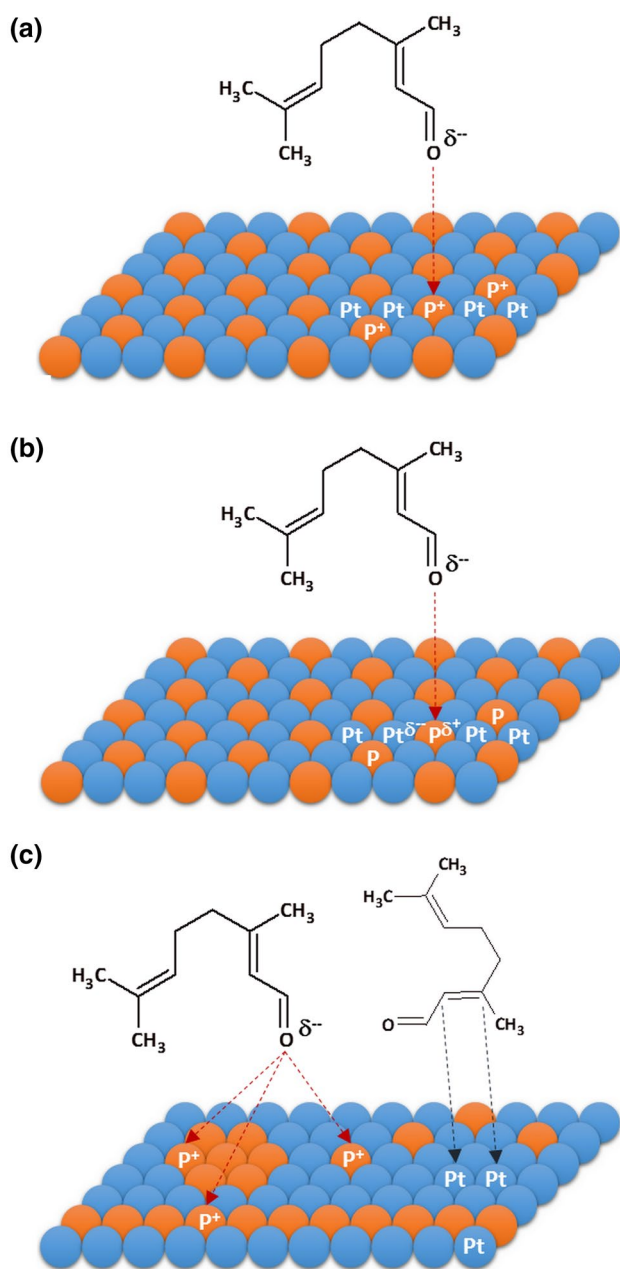
Fig. 8 Schemes of the proposed models of atom arrangements for catalysts prepared by both methods and their participation in the promotion of the C=O group. **a** Highly ordered phases with mainly promoter ionic species, **b** highly ordered phases with mainly alloyed species, **c** scarcely ordered phases with mainly promoter ionic species

UA than bimetallic RLP catalysts. The best catalytic performances were obtained with PtSn/CN–N$_2$–CI and PtIn/CN–CI (selectivity values of about 97%). For CI series, a co-reduction between Pt and the promoter (Sn, Ga, or In) induces highly ordered bimetallic phases mainly due to electronic or geometric effects, these facts promoting the selective hydrogenation of carbonyl group. Since only ionic species were found in the PtFe catalysts in the CI and RLP

series, the formation of PtFe complexes in solution suggest the presence of highly ordered PtFe bimetallic phases. RLP preparation method would not be adequate for selective hydrogenation, except for PtFe catalyts. However, the low selectivity to UA obtained with PtFe–RLPs, is due to the modification of the support under the conditions of the preparation method. For Sn, Ga and In, the formation of unsuitable bimetallic phases would be related to the poorer modification of the Pt phase by the second metal together with the presence of different atom arrangements. In this sense, the catalytic surface would have less ordered phases where the promoter is placed in the neighbouring of Pt particle islands of atoms aggregates without a significant breaking of Pt ensembles. The thermal treatment on CI catalysts produces a slight decrease in the particle size and induces changes in the morphology of bimetallic particles according to the nature of the promotor. These changes favour the formation of a more suitable bimetallic phase for selective hydrogenation in the PtSn catalyst. The thermal treatment was also effective in PtSn catalysts prepared by RLP, because only this promoter could be properly placed in the crystal lattice of the Pt particles, without a significant effect of Pt atom blocking. For PtSn and PtIn catalysts prepared by CI, reduced promoter species prevail on the bimetallic surfaces producing mainly a electronic effect with probable alloy formation. Since the amount of ionic species is very low in these catalysts, other promotion mechanism that involves alloyed species with surface polarity which would act as Lewis acid sites to promote the C=O hydrogenation was proposed. This mechanism would be more noticeable in PtSn and PtIn catalysts, but it is also present in PtGa–CI sample since these catalysts have an important amount of reduced promoter species. Taking into account that a poor or inadequate modification of the Pt metallic phase by ionic species is not effective to improve the selectivity to UA, these results also support the hypothesis that the C=O promotion mechanism is carried out by PtSn and PtIn alloyed species.

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